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16. Abstracts A summary is provided of the screening studies undertaken to evaluate the following potential agents for removing SO_2; impregnated silica gels, impregnated fly ash, hydroxides, sulfides, and sodium carbonates. The report discusses the construction and operation of a sorbent screening unit which is capable of evaluating the sorption characteristics of a given material in less than one hour. The most active sorbents found in these studies were sodium carbonate and sodium bicarbonate. The sodium carbonates were the only materials found in this study which sorbed large amounts of SO_2 at 125°C, the flue gas exit temperature. A preliminary economic evaluation of the sodium carbonate sorption systems revealed that a regenerable system for an 800 mw plant would cost about $4/ton of coal for removal of 90% of the SO_2.

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Final Phase II Report
Contract CPA-22-69-92

for

New Process Development Section
Division of Process Control Engineering Program
National Air Pollution Control Administration
Public Health Service
U. S. Department of Health, Education and Welfare

FMC Corporation
Chemical Research and Development Center
Central Research Department

December, 1970

FMC CORPORATION
CENTRAL RESEARCH DEPARTMENT
PRINCETON, NEW JERSEY

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SUMMARY AND CONCLUSIONS

A sorbent screening unit capable of evaluating the sorption characteristics of a given material in less than one hour was constructed and operated. All sorbents were evaluated in this unit using synthetic flue gas containing 0.3 percent SO_2.

The most active sorbents found in these studies were sodium carbonate and sodium bicarbonate. The latter could sorb as much as 40 percent by weight SO_2 under the test conditions.

The sodium carbonates were the only materials found in this study which sorbed large amounts of SO_2 at 125°C, the flue gas exit temperature.

Copper-impregnated silica-alumina sorbed over 15 weight percent SO_2 at 350-400°C and could be reduced with hydrogen or hydrocarbon gases at a 100-150° higher temperature.

In the short cycles studied, the copper-impregnated silica-aluminas did not lose their activity through five cycles.

None of the metals impregnated on silica gel showed the ability to oxidize SO_2 to SO_3 under conditions used in these evaluations. The only impregnated silica gels that showed good sorptive capacity were those having a strong base on the silica gel, and the sorption of SO_2 was chemisorption rather than a true physical sorption or the storing of sulfuric acid in the particles of the silica gel.

No method was found to alkalize fly ash to produce a sorbent at costs that would be competitive with limestone.

Hydroxides and sulfides were poor sorbents for SO_2. The sulfides oxidized in flue gas atmospheres and the hydroxides sorbed only over narrow temperature ranges and under conditions which made regeneration costly.

Hydrogen cation molecular sieves sorbed 4 weight percent SO_2 at 25°C and could be regenerated by heating to 200°C.

Reducing gases such as carbon monoxide and hydrogen were ineffective for removing SO_2 or sulfuric acid from carbon. No regeneration conditions were found which would prevent loss of carbon as oxides of carbon which form from reaction of the carbon with oxygen in synthetic flue gases, as well as losses due to reaction of SO_2 with carbon.

A preliminary economic evaluation of the sodium carbonate sorption systems revealed that a regenerable system for an 800 mw plant would cost about $4/ton of coal for removal of 90% of the sulfur dioxide. Major items of expense are the high capital requirements and large thermal requirements.

No economic evaluation could be made for the copper on silica-alumina system for lack of information as to the life and attrition rate of the sorbent. Based on computer analysis of the sorption rates and characteristics of this sorbent, it does not appear to be as effective as alkalized alumina and is far less effective than sodium carbonate.

RECOMMENDATIONS

Costs for an SO_2 sorption system based on sodium carbonate are higher than costs quoted for competitive systems in the literature.[56,57] It is recommended that the following studies be conducted to evaluate the possibilities of achieving major process cost reductions which would allow practical application of the high sorptive capacity of Na_2CO_3.

1. Study conversion of Na_2SO_3 and Na_2SO_4 to Na_2CO_3 by reaction with a low cost reducing gas mixture ($CO-H_2-H_2O$) in a fluidized bed, following the work of Gorbanev[69].

2. Determine whether Na_2CO_3 regenerated as in (1) above has good sorption characteristics.

3. Investigate sorber designs for sorbing SO_2 with Na_2CO_3 other than the bag filter sorber considered in this study.

If the above studies are favorable, the Na_2CO_3 sorption and desorption reactions could be operated in dry, fluidized bed systems, and capital, heat, and power costs could be reduced significantly.

INTRODUCTION

A literature survey performed under PHS Contract 22-68-67 entitled "Applicability of Inorganic Solids Other Than Oxides to the Development of New Processes for Removing SO_2 from Flue Gases" revealed process concepts that were sufficiently promising to justify laboratory work.

On the basis of this literature study, the four most promising groups of sorbents appeared to be impregnated silica gels, impregnated fly ash, hydroxides, and sulfides. The literature survey pointed up the need for an extensive evaluation of many materials for which sorption-desorption data under flue gas sorption conditions were either completely absent or were based on partial pressure, temperatures, or other parameters which were significantly different from those found in stack gas conditions. In addition, kinetic analyses based on the literature suggested that regeneration of carbon sorbents using reducing gases be studied. Carbon sorbents, it was reported, tended to burn after repeated sorption and desorption of SO_2 due to hyperactivation of the carbon. A regeneration system based on the use of reducing gases would circumvent the degradation of the carbon without impairing its other advantages.

This report summarizes the screening studies undertaken to evaluate potential agents for removing SO_2 and discusses the economics of employing a system based on two of the sorbents tested in some detail. The screening of the various sorbents was based on the following criteria:

1. The sorbent should sorb more than 5 weight percent of SO_2 in the screening test.
2. Unless the material were inexpensive enough to be discarded after one sorption, the sorbent had to be capable of being regenerated economically.
3. Because of the very large volume of gases treated it was necessary that the kinetics of the reactions of the sorbents with SO_2 be sufficiently favorable to keep the regeneration plant within reasonable size.

4. The process had to be adaptable to power plant operation. Thus, systems designed to treat stack gas had to show good SO_2 sorptive capacity at 125 to 150°C, the temperature range at which power plant gases enter the stack. However, systems capable of sorbing SO_2 up to 400°C were investigated, since these could be installed in new plants ahead of the preheater.

5. Any system selected had to show a reasonable economic potential.

The work conducted in this Phase II study was completed between June 1, 1969 and July 2, 1970.

LITERATURE SURVEY

The Phase I literature survey was evaluated and a bibliography of 580 items was included in the Final Phase I report of PHS Contract 22-68-57, dated June 1969.

The Phase I literature survey was updated with the present search covering the literature from late 1968 to early 1970. The scope was narrowed somewhat to eliminate some aspects which laboratory work had shown to have little relevance to the current study. None of the references included in the first report is repeated here. Also, patents which issued after the first compilation but which are equivalent to patents reported there were excluded.

In the earlier report, the materials were grouped in nine generic classes. The same classes are considered here, except that there were no new references to several of them.

A. GENERAL

A September 1969 review article by Cortelyou[1] evaluates processes for removal of sulfur compounds from stack gases of power plants on the bases of technical feasibility, state of development, and adaptability to United States and foreign markets. The four major processes which he considered to represent the most promising techniques are the Combustion Engineering Corporation's dry dolomite injection with wet scrubbing, the Monsanto catalytic oxidation process, the U.S. Bureau of Mines alkalized alumina process, and the Reinluft dry char absorption process. The economics of these processes were evaluated for an 800 mw power plant with a load factor of 60%. The dolomite injection process has the lowest capital investment and operating costs, and is the only process adaptable to existing power plants. However, it is associated with solid waste disposal problems. The economics of the other processes depends on the marketability of sulfuric acid.

Gas-solid interactions between sulfur dioxide in a simulated flue gas and various solid absorbents were studied by infrared spectroscopy by Burton[2] under HEW Contract PH-86-68-78. He calculated the rates at which limestone adsorbed SO_2 at 262°C, and reported an activation energy of 11.8 kcal/mole was calculated for the adsorption process. These studies combined with the recorded spectra of various limestone samples before and after exposure to SO_2 at 750 and 1800°F showed that the most probable reaction mechanism of samples exposed at 750°F was adsorption of SO_2 as sulfite and the oxidation of the sulfite to sulfate. At temperatures above 1800°F, the oxidation of sulfite to sulfate was very rapid and only sulfate was detected in the spectra of the reacted samples.

1. Mineral Products and Industrial Waste

Bench-scale testing was undertaken at the Bureau of Mines[3] to evaluate low-cost materials as dry absorbents for the removal of SO_2 from flue gas at elevated temperatures. Two of the agents found effective were western oil shale and red mud, the waste material from upgrading bauxite ore. These materials also effectively removed SO_3 after catalytic oxidation of the SO_2. Phosphate rock also reacted readily with SO_3 at elevated temperatures. These materials could be used on a once-through basis and either disposed of or, more desirably, could be transformed into a useful by-product. The oil shale and red mud also were found to be regenerable by reduction in a conceptual cyclic process.

A German patent[4] to Firma Carl Still describes the use of ashes of solid fuels and/or residues from ore dressing, containing 15-20% water and optionally 50% limestone or dolomite, for removing sulfur oxides. The materials consist of solid layers with grains of 0.5-10 mm diameter.

2. Inorganic Salts and Metals

A study of the adsorption of sulfur dioxide and oxygen on zinc sulfide was made in Japan using the E.S.R. technique[5]. The spectrum taken at 200°C indicated that the adsorbed SO_2^- species was decomposed yielding S^- radicals and O_2 molecules.

Seignole and Delafosse[6] in France investigated gaseous chemisorption on powdered cadmium sulfide. Samples of $CdS_{0.86}$ and $CdS_{0.78}$ were prepared, and the effects of adsorption of a number of gases including SO_2 on these samples on their electrical conductivity were studied as functions of temperature and gas pressures. For SO_2, physical adsorption occurred at 0-100°C and chemical adsorption at temperatures above 100°C. Differential heat of adsorption was independent of the degree of covering. Adsorption of SO_2 was partially irreversible. Owing to the strong affinity of the surface for acceptor particles as a result of the ionizable S vacancies, S^{2-} and O^{2-} were able to diffuse into the layers next to the surface active sites and were adsorbed, at least partially, by a strong chemical bond which involved transfer of electrons.

The Lummus Company has patented[7] a process for the removal of sulfur dioxide from flue gas which involves contacting the gas with a metal carbonate to form the metal sulfite and reducing the sulfite with carbon monoxide to regenerate the carbonate and produce carbon dioxide and sulfur. Suitably the carbonate is sodium or calcium carbonate.

In another patent to Spence & Sons Ltd.[8], adsorbents consisting of a carrier (Al_2O_3) combined with a basic alkali metal compound and an additive are used to remove SO_2 and other acidic gases from combustion products. The additive is chosen from Group VIII metals with atomic number over 26 (Co, Ni) or Group I, II, IV, V, VI, or VII metals or oxides or compounds of the metals. In an example, a sodium/aluminum carbonate was precipitated in the presence of cobalt, filtered, washed, dried, and ignited at 600°C. At cobalt contents of 0, 1, 2, and 4 weight percent, 12.0, 12.5, 16.5 and 19.5 g of SO_2 were adsorbed respectively per 100 g of sorbent during a 40 minute contact with a gas containing 0.2% SO_2, 6% H_2, 6.0% O_2, 15% CO_2 and the remainder N_2.

U. S. patent 3,454,355 issued to Chevron Research Company[20] reports that the efficiency of copper and promoted copper catalyst for removing SO_2 from gaseous mixtures is enhanced by the presence of small amounts of carbon monoxide. The quantity of carbon monoxide mentioned is "at least 0.75 of the stoichiometric amount necessary to reduce the sulfur dioxide and other oxidizing gases in said gaseous mixture". With flue gases, this process would require the presence of about one-half percent of CO. Most flue gases probably contain this and larger amounts of CO. It was not stated why such small quantities of CO should enhance the sorption of SO_2 from a flue gas.

3. Non-Metallic Elements

Sappok and Walker[10] studied the interaction of a typical flue gas with activated charcoal and bituminous coal char at temperatures between 600 and 800°C and atmospheric pressure. They report that the SO_2 in the flue gas interacts with the carbon to form primarily H_2S, COS and a C-S surface complex. H_2S and CO_2 break through the carbon bed much in advance of SO_2. At 800°C, sulfur retention on the bed exceeds at least

11% before SO_2 breakthrough occurs. The reaction of H_2S and COS with O_2 over activated charcoal at 100-400°C to produce sulfur, which deposits on the carbon, was also studied and found to be feasible. As a result of their study, the authors outlined a new process for the removal of SO_2 from flue gas, with the ultimate conversion of the SO_2 to elemental sulfur.

A German paper[11] states that a moving bed reactor proved suitable for the separation of SO_2 from dust-containing waste gases on adsorption cokes. The degree of desulfurization was mainly determined by the residence time of the coke. The SO_2 adsorption was not adversely affected by residence times of up to 20 hours for the cokes.

In an investigation by Japanese workers[12], sour gases containing 3.5-5.5 volume percent SO_2 and 92-95 volume percent O_2 were passed through a tubular reactor packed with granular activated carbon or that treated with concentrated H_2SO_4 at 190°C for two hours. It was found that the adsorption of SO_2 obeys the McBain equation. The adsorption properties of the carbon treated with H_2SO_4 were better than those of untreated carbon. The SO_2 adsorbed was mostly oxidized to SO_3 or H_2SO_4 above 150°C and reached maximum adsorption at 250°C. Sulfonation of carbon did not occur.

Bergwerksverband G.m.b.H. has patented a process[13] for desulfurizing combustion gases which uses a carbonaceous adsorbent impregnated with vanadium compounds and potassium, lithium, and/or barium compounds. In an example, the adsorbent was 94 g of activated pre-oxidized coal of 1-2 mm grain size, impregnated with a solution of 4.6 g of NH_4VO_3, 4.4 g of K_2SO_4, and 6.6 g of Li_2SO_4 in 50 cc of water, and dried at 110°C. Another patent to Bergwerksverband[14] covers the preparation of a molded coke agent useful for the adsorption of sulfur oxides from waste gases.

Two U. S. patents[15,16] on methods and apparatus for desulfurizing industrial waste gases by means of activated carbon were issued to Hitachi, Ltd. in 1969. In one invention, the same water is repeatedly used for washing away or desorbing from the activated carbon the sulfur oxides adsorbed thereby until the concentration of the oxides within the water reaches a predetermined value at which the water is to be discarded. In the second invention, the active carbon is regenerated repeatedly by rinsing it with water and the water can either be neutralized with alkali or passed to an acid concentrator.

A Belgian patent to Westvaco Corporation[17] covers removal and recovery of sulfur oxides from gaseous oxygen-containing streams. The gaseous stream is contacted with a carbonaceous adsorption agent at a sufficiently high temperature for the adsorption to take place, the adsorption agent is separated along with the adsorbed gases and is treated with a reducing agent at a sufficiently high temperature to reduce the adsorbate to SO_2 and/or sulfur. These are recovered, and the adsorption agent is recycled.

The desulfurization of oxygen-containing combustion gas is also the subject of a German patent to Kogyokaihatsu Kenkyusho[18]. Sulfur oxides are removed by adsorption on activated charcoal. The combustion gas is divided into two streams, one being continuously fed to washed, undried activated charcoal and then being mixed with the other stream. The mixed streams are then passed through dried activated charcoal.

In 1967 Chemiebau Dr. A. Zieren G.m.b.H and Co. K.G., acquired a majority interest in Reinluft G.m.b.H and instituted studies to overcome its deficiencies[19,20]. The changes included (1) separation of the adsorber and desorber sections, (2) compartmentalizing the adsorber section to prevent segregation of coke sizes, (3) a filling-level control which ensures uniform grain distribution and quantity of coke in each compartment to balance flow resistances of all layers, and (4) controlled cooling of coke in the conveyors between the adsorber and desorber sections to prevent autoignition of the coke. Pilot plant studies indicate these changes have eliminated coke-burning problems.

4. Oxides of Non-Metals

The possibility of using silica gels for the removal of sulfur dioxide from industrial wastes was investigated in Russia[21]. Studies were made on KSM-5 type silica gel by using steam and SO_2 diluted with nitrogen. Steam absorption isotherms determined at 20, 40 and 60°C indicated minimum dependence of adsorption on temperature. Isotherms of SO_2 adsorption were studied in the range of 25-200°C. A high degree of adsorption was noted at higher temperatures (100-200°C). This result was partly explained on the basis of oxidation of part of the SO_2 by 0.5% oxygen impurity in the nitrogen to SO_3 which is readily adsorbed on silica gel.

Investigation of the adsorption dynamics of SO_2 diluted by nitrogen to 0.5% (by volume) showed the linear dependence of the height of the absorbent layer on the gas velocity.

5. Hydroxides

A recent U. S. patent assigned to Grillo-Werke A.-G[22] covers a process for the recovery of sulfur or sulfur-containing compounds, or a mixture thereof, from an industrial gas. The gas is contacted with an absorbent comprising (1) an oxide, hydrated oxide, or hydroxide of aluminum, zinc, iron, or manganese, or a mixture of any two or more of such compounds, and (2) an oxide or hydroxide of an alkali metal or an alkaline earth metal or a mixture of any two or more such compounds.

SECTION I - EXPERIMENTAL APPARATUS

A. SORBENT SCREENING UNIT

All sorbents were evaluated in the sorbent screening unit. This unit was designed to screen potential SO_2-adsorbing materials in one hour using moist synthetic flue gas to approximate actual compositions and flow rates found in power plant flues. Normally, one liter per minute of synthetic flue gas was passed through one gram samples. In a holder with a cross-sectional area of 1 square centimeter, this gave a flow velocity of approximately 17 cm/sec or 0.6 ft per second. A range of flows from 250 cc to 3 liters per minute could be tested readily.

Synthetic flue gas was made by blending four individual streams of oxygen, nitrogen, a combined stream of CO_2 and SO_2 and a stream of 1% nitric oxide in nitrogen. The flow diagram of the panelboard is shown in Figure 1. The combined stream of SO_2 and CO_2 was used to obtain a more accurate metering in the desired 3000 to 3500 ppm SO_2 range. Moisture was added to the gas streams by passing only the oxygen and nitrogen streams through the water bubbler, which was kept at a temperature which allowed sufficient water to be vaporized to give the entire gas mixture a 4 to 6 mol percent water content. A typical mass spectrographic analysis showed the dried gas mixture to contain 82.7% nitrogen, 14.9% CO_2, 3.0% O_2, and 0.35% SO_2. The test gas mixture originally contained 6 mol percent water, since this was the calculated water content of flue gas from dry coals having 6% hydrogen and being burnt with 20% excess of air. However, the water content was reduced to 4 mol percent in later studies at the suggestion of NAPCA personnel. Gas flows were piped so that gas could bypass the water bubbler and/or the sample holder and go straight to the SO_2 analyzer.

The operator's panelboard with its pressure control regulators and rotameters is shown in Figure 2. The panelboard was fabricated from heavy gauge sheet aluminum, supported by an angle iron frame, and was mounted on a laboratory bench top adjacent to the sorption unit. Figure 2 shows three rotameters for the nitrogen, oxygen and CO-SO_2 gas stream. A fourth rotameter for a 1% nitric oxide in nitrogen stream was also mounted but is not shown in the figure.

Each gas stream was metered through Matheson series 620 rotameters. Flows were hand-controlled by adjusting needle

Figure 1

Flow Diagram of Panel Board for
Sulfur Dioxide Adsorption Apparatus

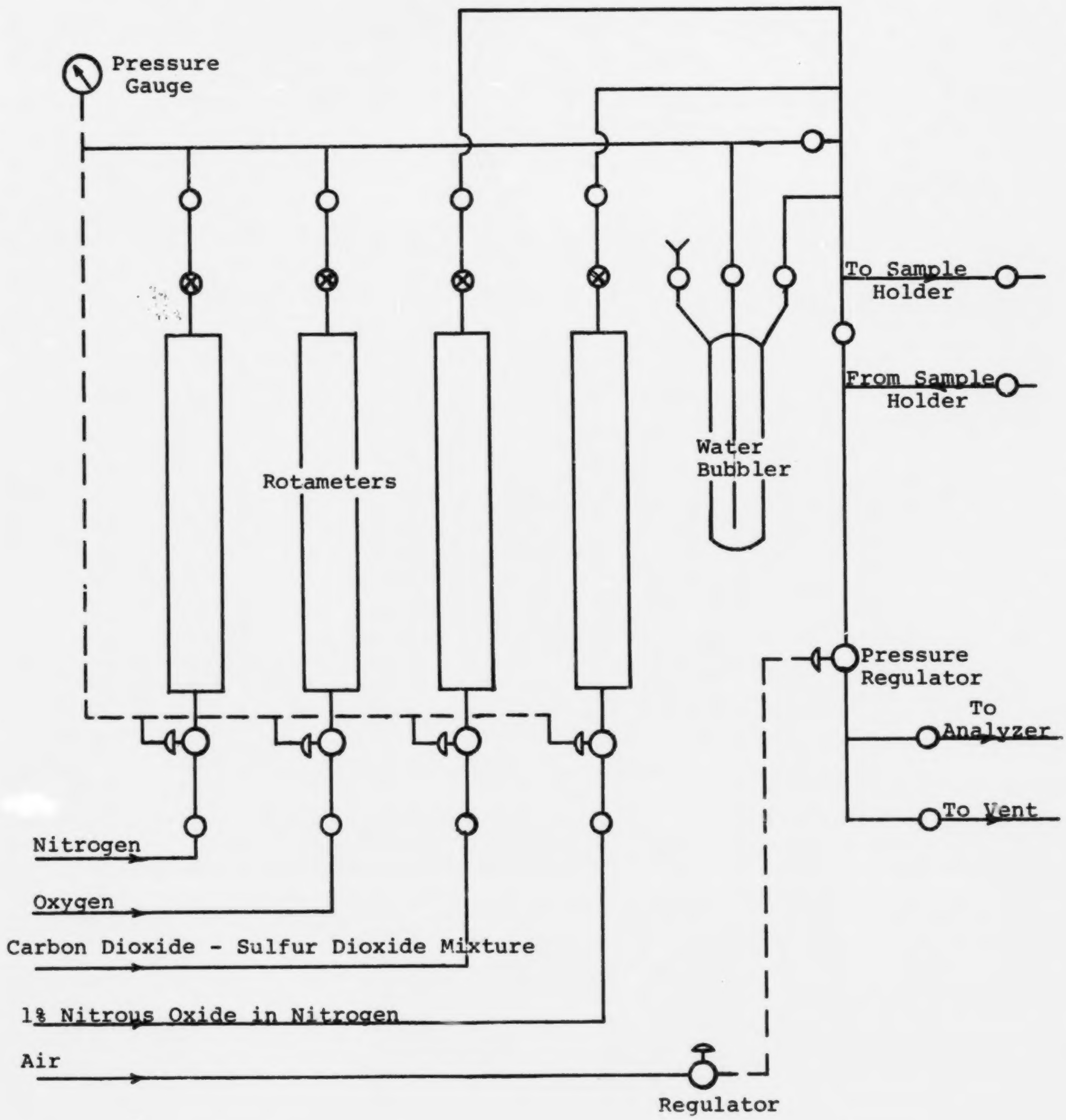
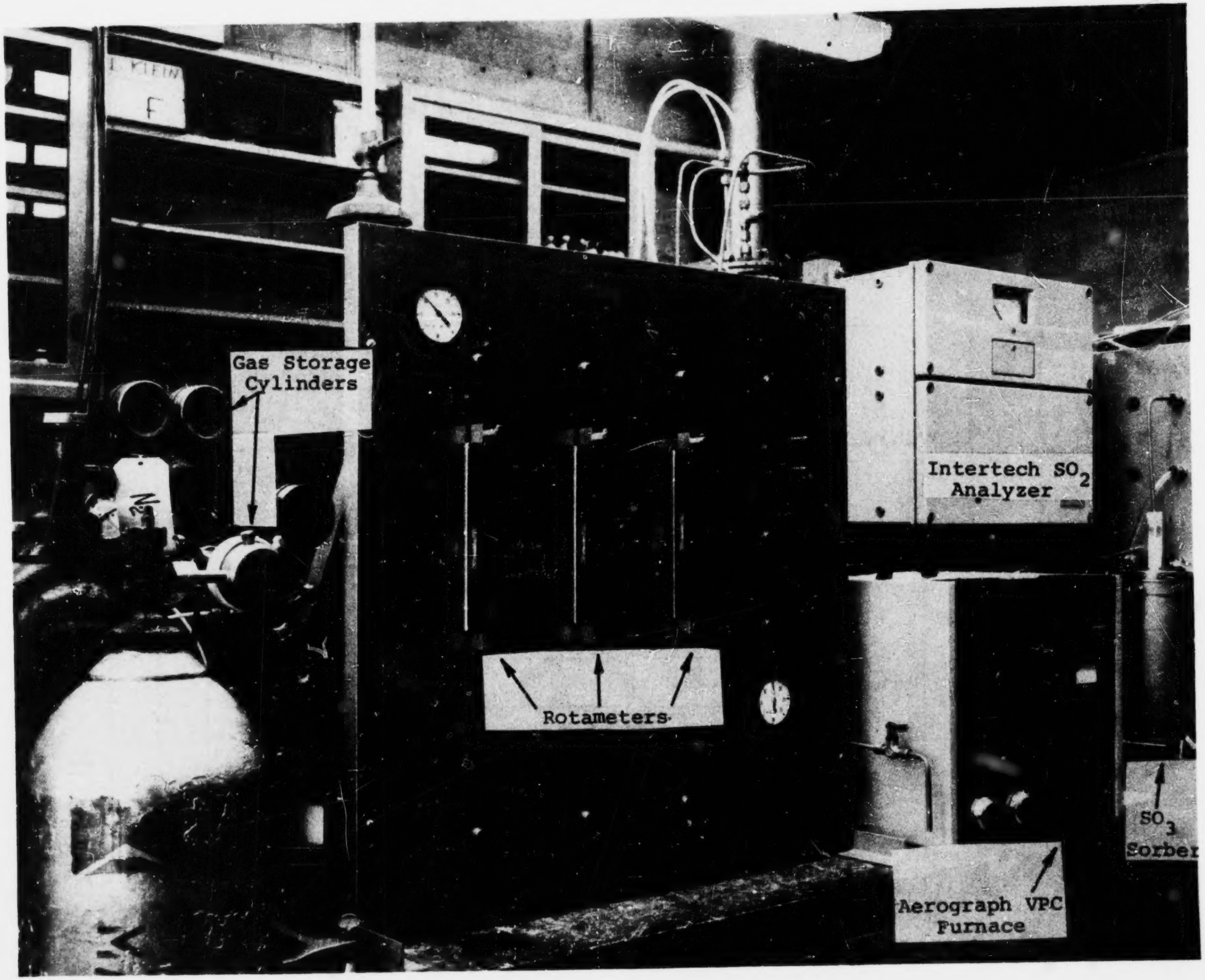

Pressure Gauge
Rotameters
Water Bubbler
To Sample Holder
From Sample Holder
Pressure Regulator
To Analyzer
To Vent
Nitrogen
Oxygen
Carbon Dioxide - Sulfur Dioxide Mixture
1% Nitrous Oxide in Nitrogen
Air
Regulator

FIGURE 2 Sorbent Screening Unit Panelboard


Gas Storage Cylinders
N_2
Rotameters
Intertech SO_2 Analyzer
Aerograph VPC Furnace
SO_3 Sorber

valves. The flows were started and stopped by Hoke Toggle valves placed above and below the flow meters.

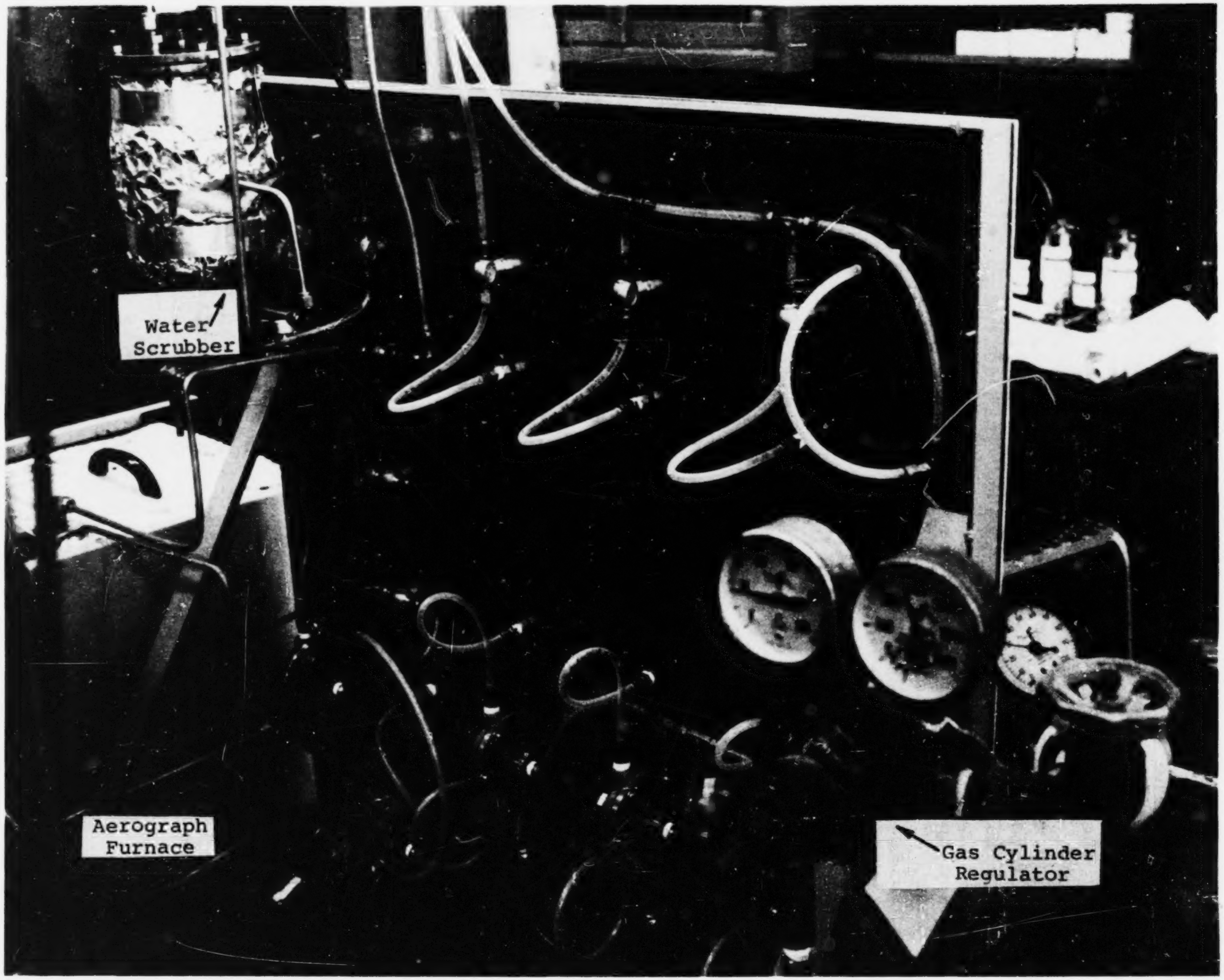
The gas cylinders were placed at the left of the panelboard. Figure 3 shows the rear of the panelboard. Polyethylene tubing was used to carry the individual gases to the pressure regulators, rotameters and water scrubbers. However, moist synthetic flue gas passed through stainless steel tubing only. The water scrubber, shown in the upper left hand corner of the diagram, was fabricated out of stainless steel pipe 6" long. The scrubber was heated by an electric tape and insulated with fiberglass insulation held inside an aluminum foil wrapping. The scrubber had a drain pipe which maintained a nearly constant height of water inside the bubbler so that the back pressure remained constant.

The panelboard contained two pressure gauges (Figure 2). The gauge in the upper left hand corner indicated the manifold pressure, and the gauge in the lower right hand corner indicated the pressure of the gases entering the sample holder. This pressure gauge also detected build-up of pressure within the sorbent bed. Toggle switches placed above and below the rotameters gave rapid control of individual gas flows.

The unit at the right of the panelboard on the desk top in Figure 2 is an oven of an Aerograph VPC furnace. This is a Model 1200 gas chromatographic oven that was purchased without the electrometer or detection system which is normally an integral part of a gas chromatograph. This unit had a furnace area 9" x 9" x 6" in which the preheater and sample holder were mounted. The preheater consisted of a 10-ft section of 1/4" stainless steel tubing coiled around the heater of the GC oven. This preheater insured that the gas reached the indicated furnace temperature before it passed downflow through the sample holder.

The sample holder was a vertically mounted stainless steel tube 4" long and 1/2" in diameter. The sample was supported on a sintered steel plate near the bottom of the sample holder. Special stainless steel fittings permitted the sample holder to be installed and removed rapidly from the unit even at high temperatures. A thermocouple extended through the top of the sample holder to measure the temperature inside the sample bed and another thermocouple was placed on the outside of the sample holder. The two thermocouples

FIGURE 3 Rear View of Sorbent Unit Panelboard


Water Scrubber
Aerograph Furnace
Gas Cylinder Regulator

rarely varied by more than 10°C at all temperatures up to 400°C.

Gases leaving the sample holder passed successively through a solid SO_3 adsorbent, a refrigerated unit which condensed the bulk of the moisture in the sample, and then to an Intertech nondispersive Infra-Red SO_2 analyzer. The removal of the SO_3 and the bulk of the water improved the accuracy of the SO_2 determination. The SO_3 sorber and SO_2 analyzer are shown at the right and above the Aerograph furnace, respectively. Figure 4 shows the cooling unit that removed the water for the SO_2 analyzer and the Sargent Recorder on which the concentration of SO_2 in the gas was recorded continuously. The terminal at the lower right hand corner of the Sargent Recorder was used to connect the recorder to a data logger for calculation of the sorption result by computer, as described below.

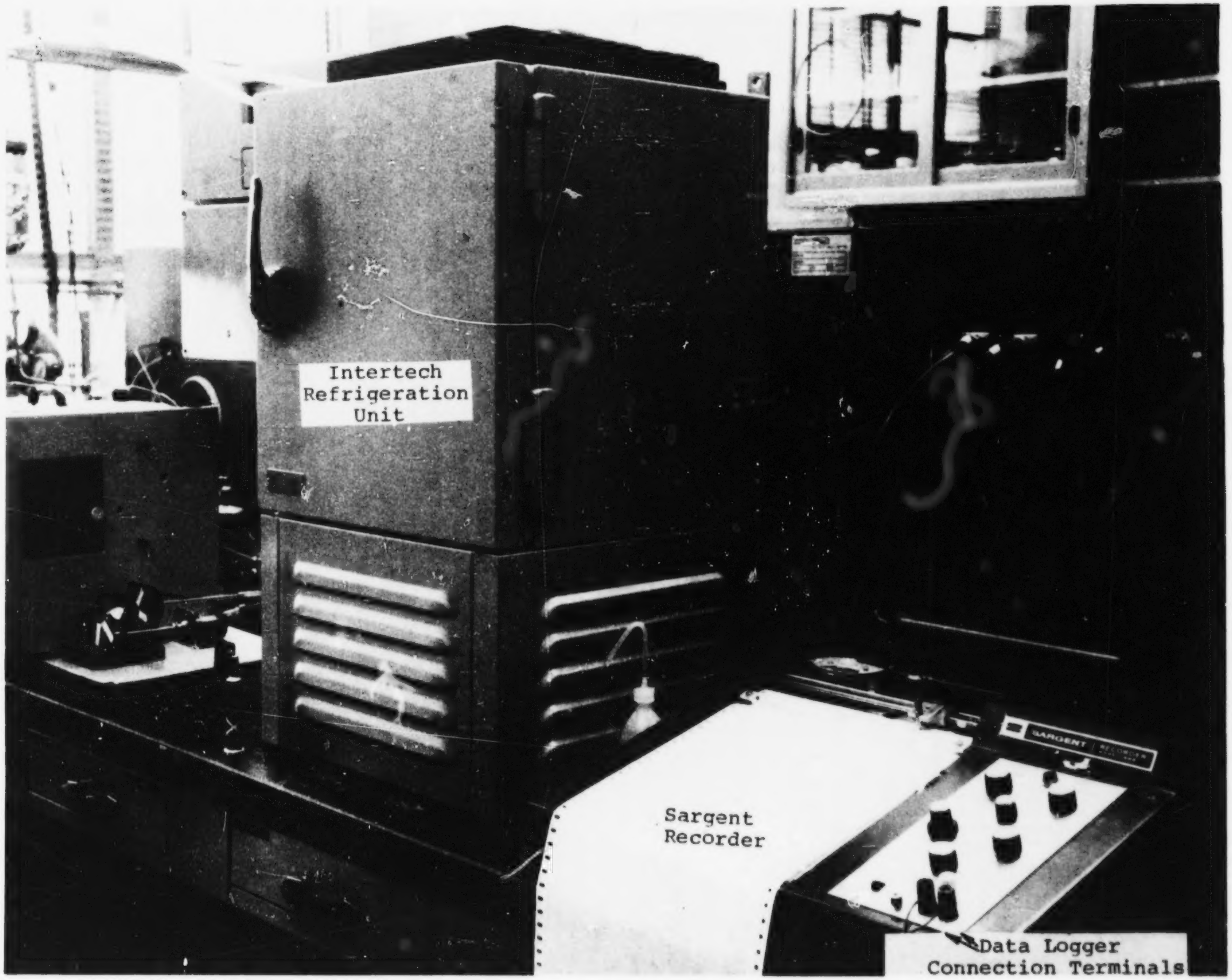
1. Operation

The material to be tested was placed in the sample holder of the screening unit and the thermocouple was placed inside the bed of sorbent. The sample holder was connected to the preheater coil inside the heating unit and the system was pressure tested for leaks. When sorptions were made at elevated temperatures, the sample was heated while the gas flow calibrations were being made.

To calibrate the unit, all rotameters were checked while the sample bypass was open so that no gas passed through the sample. The recorder was started and two baselines were obtained. The upper baseline represented the line obtained for 3500 ppm of SO_2 in the synthetic flue gas sample. The lower line was that obtained with the SO_2-CO_2 stream cut out of the feed. The upper line served as a check before each run to insure that all gas flows were correct. The lower line, obtained with oxygen and nitrogen only, insured that all lines were swept free of SO_2 before the actual sorption was made.

Once the lower baseline was established, the SO_2-CO_2 stream was cut into the moist oxygen-nitrogen gas stream and the synthetic flue gas sample was passed through the sample which had been heated to the desired temperature. The sorption was continued until the recorder indicated that sorption of SO_2 had ceased or until the run was stopped at some predetermined breakthrough. At this point the valves

FIGURE 4 Sorbent Screening Unit Refrigeration and Data Logger



Intertech
Refrigeration
Unit
Sargent
Recorder
Data Logger
Connection Terminals

leading to the sample holder were closed and the sample by-pass valves were opened. This allowed the synthetic flue gas mixture to pass directly to the SO_2 analyzer and served as a check to insure that the SO_2 concentration had not changed during the run. Once this was established, the CO_2-SO_2 stream was turned off and the system was flushed with oxygen and nitrogen until the original SO_2-free base line was reached. This flushing generally required less than 5 minutes. The sample holder was cooled to room temperature and prepared for the next run.

Normally, sorbents were sized to -200 + 325 mesh cuts. With this particle size it was usually possible to operate with a back pressure of 20 pounds psig. However, some alkaline sorbents developed higher back pressures on contact with moist flue gas. Back pressures in excess of 20 psig during a run caused erroneous gas flows and changes in the concentration of SO_2. In such cases, coarser sample sizes were used. Size cuts used included -30 + 50, -100 + 200, and -60 + 100 mesh fractions. Replacing a -200 + 325 mesh fraction with a -60 + 100 fraction normally affected the sorptive capacity of materials by less than 1 weight percent, unless noted otherwise in the tabulation of results.

Early studies showed that a significant time lag occurred between the time when SO_2 was passed into the unit and when it was detected by the IR analyzer. This time lag was determined by making a series of calibration curves in which the synthetic flue gas mixture was passed through a sample of sand that had been heated to 700°C to destroy any contaminants or reactants which might be present. Typical calibration curves, presented in Figure 5, show that the time interval between the time when the SO_2 was charged and when it was detected on the recorder varied inversely with the flow rate, being much greater at the lowest flow rates. This delay in SO_2 breakthrough could have contributed a substantial error to some measured SO_2 sorption results. However, the effect of this time lag in SO_2 breakthrough was eliminated by a computer program which deducted the curves obtained in the calibration from the adsorption curves obtained with each sample.[1]

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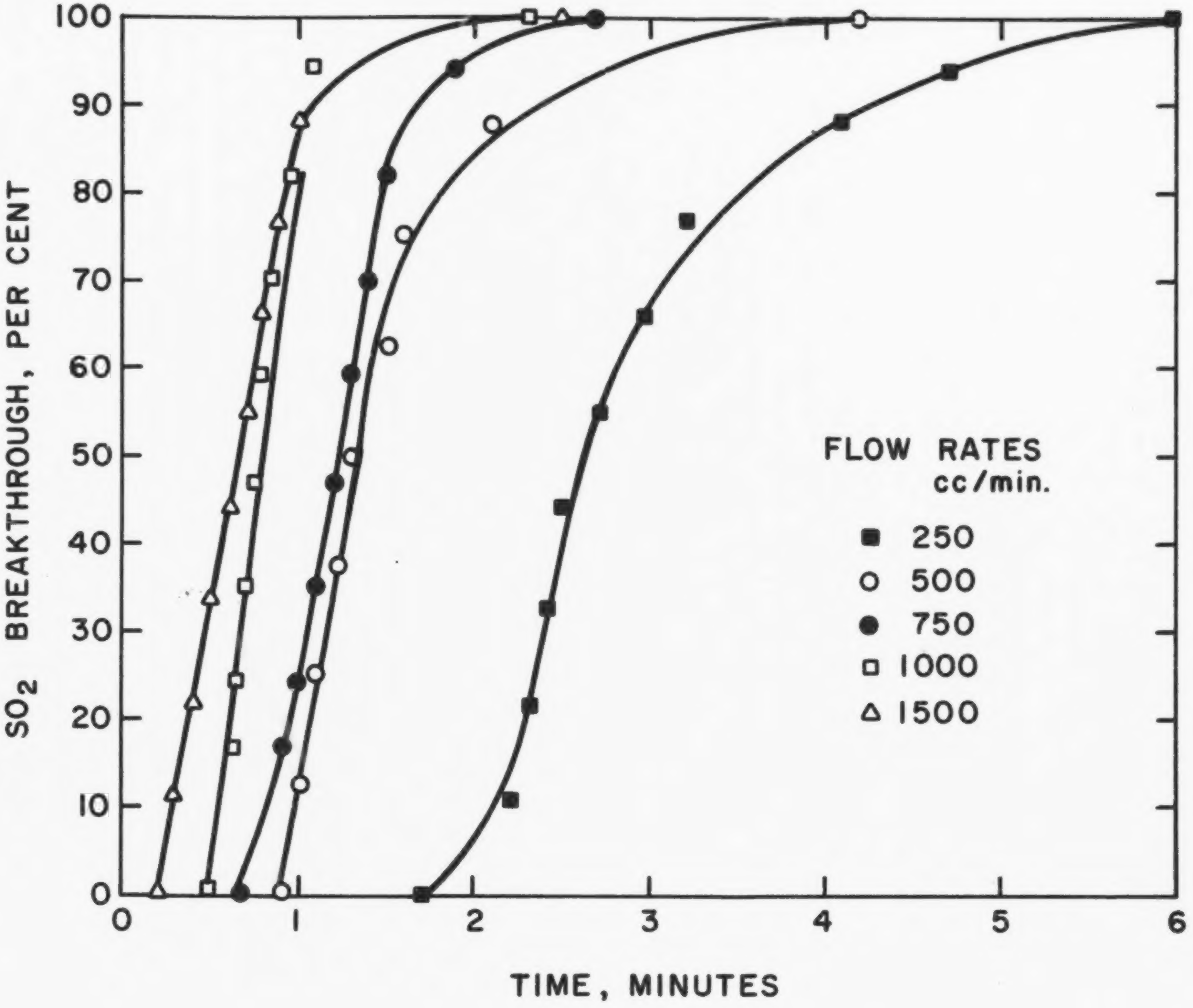
[1] The computer program is described in detail in Appendix 1, pages I-1 through I-13.

FIGURE 5

SCREENING UNIT CALIBRATION CURVES FOR SO_2 BREAKTHROUGH AT 100°C



For this computer program, the SO_2 breakthrough data were punched on paper tape by a data logger attached to the Sargent temperature recorder. From this tape, the computer program performed the following:

a. It read the paper tape for each blank run and generated a relationship for the dead run of the experimental system with an inert catalyst. Lag-time relationships which had first been generated for each set of experimental conditions studied were used to correct the active sorbent runs for the dead time present in the system.

b. After correction for the dead time by using the function described above, the corrected SO_2 exit concentration-time data were integrated numerically to calculate the cumulative SO_2 adsorbed. Sorbent loading was obtained by dividing this cumulative SO_2 adsorbed by the gross weight of sorbent charged. The instantaneous rate of sorption was calculated directly from the corrected concentration-time data. The output consisted of the cumulative weight of SO_2 sorbed, the sorbent loading, and the instantaneous sorption rate for each time recorded. The saturation catalyst loading could be determined by extrapolating a curve of catalyst loading vs. the instantaneous rate to 0 slope. This was used in many runs with moderately active sorbents or with curves having a long tail, since the time required to completely saturate such sorbents could be quite long. With such sorbents, the runs were discontinued when SO_2 breakthrough exceeded 75 to 80 weight percent of the SO_2 charged and the 100% loading value was calculated by the computer program.

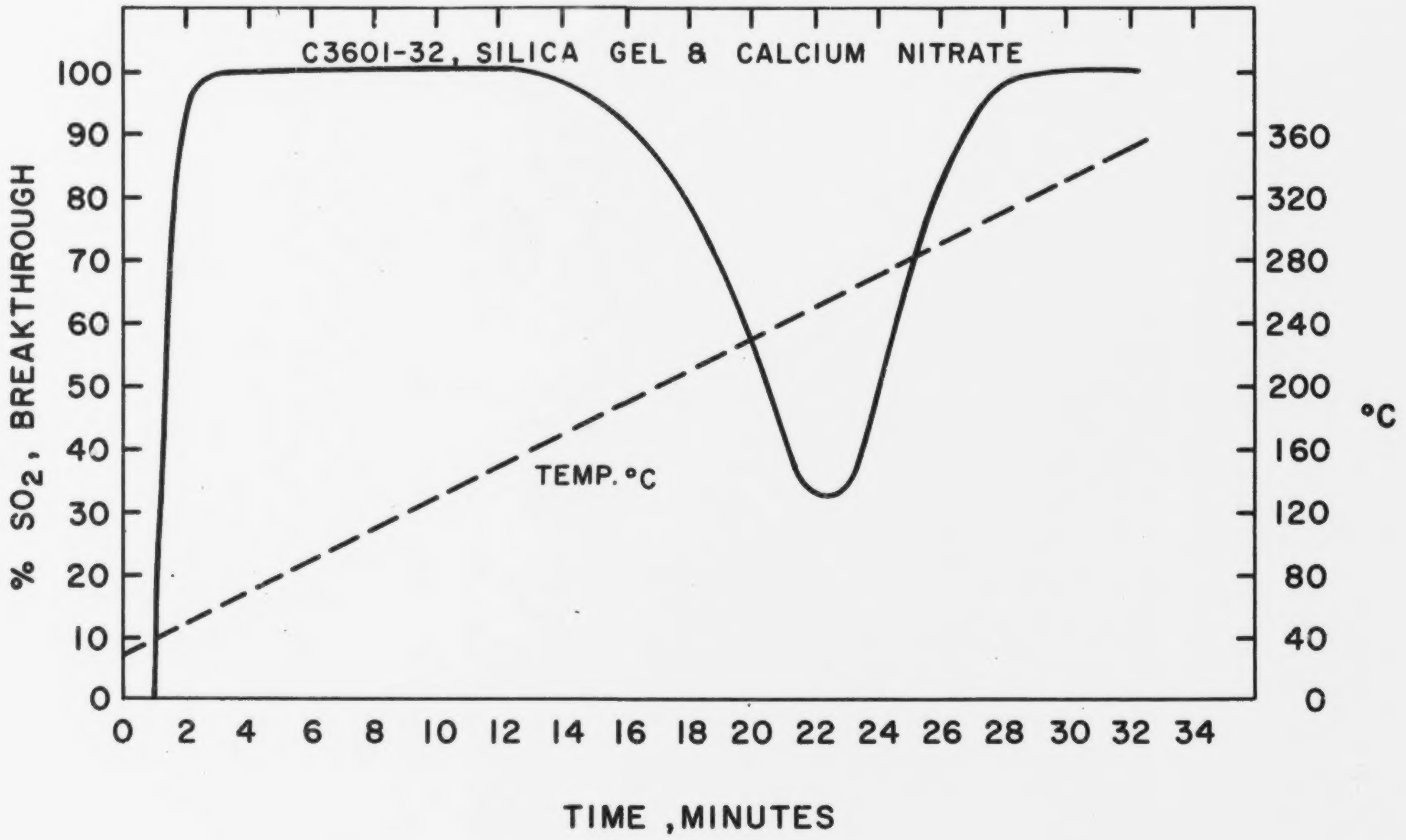
2. Sorbent Evaluation

With a new sorbent, the preliminary screening runs were usually variable temperature runs in which samples were heated at a fixed rate from 25 to 400°C. Figure 6 is an example of an SO_2 breakthrough curve obtained at a constant heating rate of 10°C per minute with a silica gel impregnated with calcium. This material sorbed almost no SO_2 below 150°C, as evidenced by the immediate and complete SO_2 breakthrough after two minutes on stream. However, between 160 and 300°C this

FIGURE 6

SORPTION OF SO_2 ON A CALCIUM-IMPREGNATED SILICA GEL

HEATED AT 10°C/MINUTE



material sorbed SO_2 with maximum sorption, or minimum SO_2 breakthrough, occurring at approximately 250°C. Such sorption temperature profiles were used to determine temperature regions favoring sorption. Isothermal runs were then made with the materials in the temperature regions at which sorption was indicated.

Figure 7 shows the three general types of isothermal curves obtained in this work. Active carbon, which is a good sorbent, sorbed essentially all SO_2 for periods of 6 to 8 minutes and then gave a breakthrough of SO_2 which increased progressively with time.

The curve for run 3601-21 is the curve for a barium nitrate impregnated silica gel with no SO_2 sorption capacity which gave a breakthrough of 90% in less than 2 minutes. (These raw data were not corrected for the lag-time effect described above.) The curve for run 3601-36 also showed rapid SO_2 breakthrough. However, the sorbent retained a considerable sorptive capacity throughout the period shown. Thus, the SO_2 breakthrough was only 25% after 3 minutes, 50% after 7 minutes, and 70% after 18 minutes.

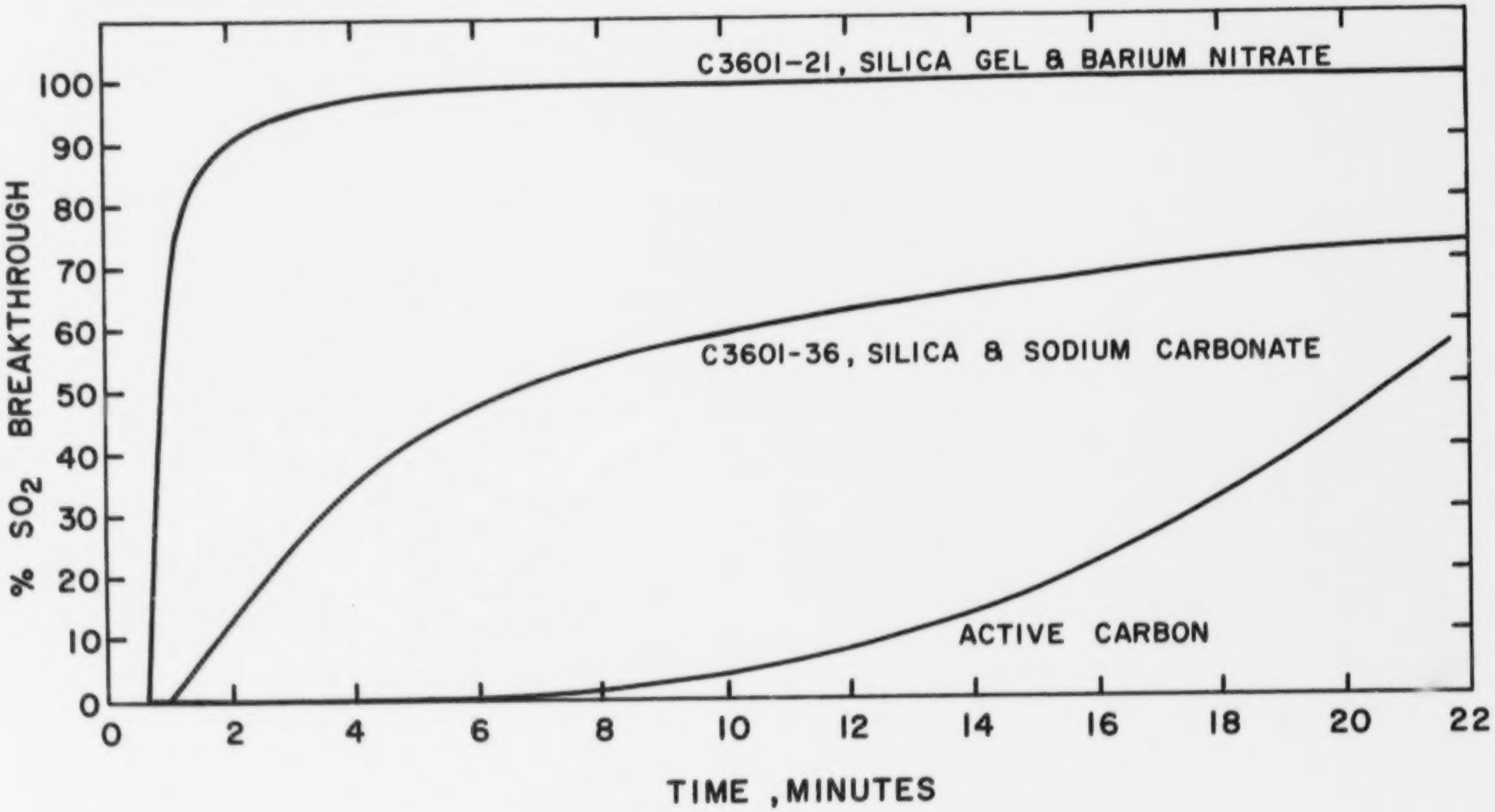
B. HIGH TEMPERATURE SORPTION TEST SYSTEM

Some studies were conducted in a high temperature test system which was capable of sorption or desorption runs at temperatures as high as 1200°C. Two reactors made of stainless steel tubing were used. One reactor was 1/2" o.d., the same size and with the same gas flow characteristics as that used in the holder of the sorbent screening unit. The second reactor, made of 1" i.d. stainless steel tubing, was used for studying large samples. Both reactors had stainless steel sample supports approximately 3" above the bottom of the 12" long Hoskins-type furnace in which the reactors were heated to the reaction temperature. Both reactor systems could be placed in the sorbent screening system in place of the sorbent holder and the gas chromatographic furnace, in which case the same gas manifold and SO_2 detector described above could be used. Alternatively, either reactor could be used with a synthetic flue gas mixture which was blended by mixing moist air with a mixture of gas containing 14% CO_2, 0.4% SO_2, and 85.4% nitrogen. The quantity of air added gave the combined gas stream an oxygen content of 3%. The air was passed through water heated to that temperature which added 4 mol percent of water to the synthetic flue gas mixture.

FIGURE 7

SAMPLE SO_2 SORPTION

DATA READOUT
AT 150°C



When the high temperature test systems were not used with the Intertech SO_2 analyzer, SO_2 sorption was determined by iodine titration. The SO_2 in the exit gas from the reactor was titrated with iodine, which was added at the rate which just reacted with the evolved SO_2. Thus, iodine losses through vaporization were eliminated, and accurate information on both the rate and amount of SO_2 sorbed on known weights of solids could be obtained. Correlations between the results obtained by the SO_2 analyzer and iodine titrations were excellent.

The 1" i.d. sorption reactor held over 20 grams of sorbent in the "hot zone" of the furnace and was also used for preparing sorbents in a reducing atmosphere.

SECTION II - EXPERIMENTAL RESULTS AND DISCUSSION

The laboratory screening program conducted during the major period of this program was instituted to evaluate SO_2 sorption-desorption characteristics of potential new candidate materials for which only limited laboratory data were found or for which the data were too sketchy to permit an evaluation of sorbent effectiveness. The materials tested are discussed in the 9 primary classes into which the inorganic materials were classified in the first phase report.

A. CLAYS

Bentonites were reported to be sorbents for oxides of sulfur.[23,24] The latter reference states that the heat of adsorption of water on an activated bentonite is two to three times that of the oxides of sulfur. Because the water content of the flue gas is so much higher than that of the sulfur oxides, it was thought water would be adsorbed preferentially rather than the oxides of sulfur. Therefore, clays were not considered to be promising adsorbents for SO_2. However, because of bentonite's relatively low cost and inertness to oxides of sulfur, this conclusion was verified as part of the overall screening development program.

Two samples of bentonite from International Minerals Company were evaluated and the results are shown in Table I.

TABLE I

Sorption of SO_2 on Bentonite

Sample No.	Material	Properties	Screening Temp. °C	SO_2 Sorbed Wt. %
RO-1	Bentonite	58.1% SiO_2, 19.6% Al_2O_3, 3.1% Fe_2O_3, 2.7% MgO, 1.7% Na_2O, 0.3% H_2O	125	2
RO-2	Bentonite	59.1% SiO_2, 19.6% Al_2O_3, 6.0% Fe_2O_3, 5.5% MgO, 1.7% CaO	125	<1
RO-3	Bentonite	10% Na_2CO_3 on +100 mesh RO-1 Bentonite	125	1

The RO-1 bentonite, a more basic material, sorbed 2 weight percent SO_2; the calcium based RO-2 bentonite sorbed less than 1 weight percent SO_2.

RO-3 was a sample of bentonite on which 10 weight percent sodium carbonate was impregnated. Because of its ability to withstand the 1000-1100°F temperatures that were needed to regenerate sodium sulfite by reduction, bentonite was viewed as a potential carrier for sodium carbonate. At 125°C, sample RO-3 was a poor SO_2 sorbent.

The poor SO_2 sorption properties of the alkali-impregnated bentonite probably stemmed from its relatively low surface area, since studies described below showed that the best supports for sodium carbonate were substrates having large surface areas.

B. MINERAL PRODUCTS

A U. S. Patent reported that dried chrysotile asbestos sorbed up to 3 weight percent of sulfur.[25] Two samples of chrysotile asbestos obtained from the Johns Manville Company and from Union Carbide were evaluated and found to sorb less than 0.5 weight percent of SO_2 at 125°C as shown in Table II.

TABLE II

Sorption of SO_2 on Mineral Products

Sample No.	Mineral Products	Screening Temp. °C	SO_2 Sorbed Wt. %
R1-4	Chrysotile Asbestos J. M. Paperbestos #5	125	0.4
R1-5	Chrysotile Asbestos Union Carbide RO-144	125	0.3
R1-1	FMC Aviboard-91 Proprietary FMC Product Prepared from Asbestos and Silica. Density 7.14, Surface Area 124 m^2/g	25-350	1
	FMC Phosphate Rock	25-300	1

A sample of Aviboard-91, a proprietary FMC product prepared from asbestos and silica, was evaluated. Although this material had a surface area of 124 m^2/g, it proved to be a poor SO_2 sorbent, as less than 1 weight percent SO_2 was sorbed in a scanning run made between 25 to 350°C.

Phosphate rock was evaluated for SO_2 sorptive capacity to check statements in the literature concerning its ability to sorb SO_2.[26,27] This rock sorbed only traces of SO_2.

C. INDUSTRIAL BY-PRODUCTS

1. Alkalized Fly Ash

a. Introduction

In Germany, the Still process uses hydrated basic lignite ash to adsorb SO_2.[28] The lignite ash may or may not be augmented or supplanted with hydrated lime. The process operates in the temperature range between 200 and 850°C. Oxygen and carbon dioxide do not interfere with the sorption operation, according to the description of the Still process. The reaction occurs in a transport bed and is primily the reaction of calcium hydroxide with SO_2. Thermochemical data indicate that the reaction is highly favorable and that the temperature of operation is limited only by the decomposition of the calcium hydroxide, which is above 580°C.

Thermal regeneration of the SO_2-laden ash is difficult, because part of the calcium sulfite that forms is oxidized and disproportionates to calcium sulfate and calcium sulfide. Thus, some of the SO_2 sorption capacity of the lime or calcium oxide would be lost. However, the lime is inexpensive enough so that partial regeneration may be practical or the spent adsorbent may be discarded entirely. A somewhat similar process was described by Herzog[29] who combined SO_2 with the basic constituents of ash. His SO_2 removal reaction, also based on the reaction of calcium oxide with SO_2, has been described as a promising commercial development in East Germany.

The use of an alkalized fly ash to remove sulfur dioxide appeared to have considerable merit. Many fly ashes are basic and their natural basicity could be used to remove sulfur dioxide. In addition, the basicity might have been enhanced by modifying the fly ash to make it a support for a hydrated lime which would react with the oxides of sulfur. Such an alkalized fly ash would be similar to the ashes used in the Still process, but would be more generally available than the lignite ash which the latter process uses and which is available only in rather limited geographic areas. If used on a once-through basis, the difficulties encountered in regenerating alkalized fly ash would not be a factor.

b. Experimental

Two samples of fly ash were obtained from nearby power plants. Anthracite fly ash was obtained from the Uniroyal Company at Parsippany, New Jersey. This material was quite uniform and had little extraneous matter. The sample of bituminous fly ash, obtained from the Princeton University boiler house, was derived from Coal Mountain #12 coal from southern West Virginia. This is a very clean coal, containing only 6% ash and 0.95% sulfur, as received in Princeton. However, the sample of fly ash was contaminated with about 35% of carbon. The Princeton power plant uses a Vibragrate Stoker in which air is blown through a spreading grate stoker, and this combustion air entrains considerable carbon along with the fly ash. No attempt was made to remove the carbon from the fly ash particles in these studies.

Both fly ashes were evaluated in scanning runs at temperatures between 25 and 350°C (see Table III) and neither sorbed SO_2 in significant amounts. After impregnation with 1 to 5% each of lime and sodium carbonate, all alkalized samples showed sorptions of less than 1 weight percent of SO_2. The low sorptive capacity of the Na_2CO_3-impregnated fly ashes was attributed to the low surface area of the material, and, in the case of the lime, to its insolubility.

In runs R2-12 and R2-13 in Table III, about 8% of calcium was impregnated on the two fly ashes by wetting the ash with a concentrated solution of calcium formate in water and then drying the products in an oven at 140°C. These materials had good sorptive capacity at 350°C. Thus, the impregnated fly ashes made from calcium formate sorbed 10.8 and 17.9 weight percent of SO_2. The computer sorption data for these materials at 350°C are shown in Tables IV and V. The active species in these sorbents was calcium oxide which was formed by the thermal decomposition of calcium formate at or below the sorption temperature studied. At 125°C where decomposition of calcium formate did not occur, these materials sorbed less than 3% SO_2.

TABLE III

Sorption of SO_2 on Industrial By-Products

Catalyst Number	Description	Sorption Temp. °C	SO_2 Sorbed Wt. %
R2-0	Uniroyal (Anthracite) Fly Ash	25-350	<1
R2-6	Princeton (Bituminous) Fly Ash	25-350	<1
R2-9	Princeton Fly Ash Impregnated 10 times with Saturated $Ca(OH)_2$ Solution	20-350	1
R2-11	Uniroyal Fly Ash Impregnated 10 times with Saturated $Ca(OH)_2$ Solution	20-350	<1
R2-12	Calcium Formate Impregnated Uniroyal Fly Ash, 7.3% Ca	350	10.8
R2-13	Calcium Formate Impregnated Princeton Fly Ash, 8.4% Ca	350	17.9
R2-24	10 g. P.F.A.,* 10 g. $Ca(OH)_2$, 5 g. Fisher Na_2SiO_3 Solution, 20 cc H_2O. Dried overnight at room temperature.		1.6
R2-25	Same as above, dried 2 days at room temperature.		2.2
R2-25A	Same as above, dried 5 days at room temperature.		0.9
R2-28	10 g. P.F.A.,* 10 g. $Ca(OH)_2$, 45 cc H_2O, boiled 30 minutes, dried 3 days at room temperature.		1.9

*Princeton University boiler fly ash.

NOT REPRODUCIBLE

TABLE IV

RUN 10 SORBENT RZ-12 (7% CALCIUM ON ANTHRACITE FLY ASH)
ONE GRAM, TEMP. 350 DEG. C, FLOW 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
1.91	0.00	0.100E-01	0.009	0.088
2.25	634.17	0.819E-02	0.012	0.116
2.58	1244.26	0.645E-02	0.015	0.138
2.91	1605.90	0.541E-02	0.017	0.156
3.25	1830.27	0.477E-02	0.018	0.172
3.58	1974.77	0.436E-02	0.020	0.186
3.91	2087.15	0.404E-02	0.021	0.199
4.25	2143.34	0.387E-02	0.023	0.212
8.91	2183.48	0.376E-02	0.040	0.376
9.91	2303.59	0.342E-02	0.044	0.409
10.91	2392.20	0.316E-02	0.047	0.439
11.91	2472.47	0.293E-02	0.050	0.467
12.91	2560.77	0.268E-02	0.053	0.493
13.91	2616.97	0.252E-02	0.056	0.517
15.91	2721.33	0.222E-02	0.060	0.561
16.91	2769.49	0.208E-02	0.063	0.581
17.91	2817.66	0.195E-02	0.065	0.600
18.91	2873.85	0.179E-02	0.066	0.617
19.91	2913.99	0.167E-02	0.06	0.633
20.91	2954.12	0.156E-02	0.070	0.648
21.91	2994.26	0.144E-02	0.071	0.662
22.91	3034.40	0.133E-02	0.073	0.674
23.91	3066.31	0.123E-02	0.074	0.686
25.91	3138.76	0.103E-02	0.076	0.707
26.91	3154.91	0.987E-03	0.077	0.717
28.91	3202.98	0.849E-03	0.079	0.733
32.91	3275.22	0.642E-03	0.082	0.761
33.91	3291.28	0.596E-03	0.083	0.767
34.91	3299.31	0.573E-03	0.033	0.772
52.65	3500.00	0.000E 00	0.108	1.000

TABLE V

NOT REPRODUCIBLE

RUN 41 SORBENT RZ-13(8% CALCIUM ON BITUMINOUS FLY ASH)
ONE GRAM, TEMP. 350 DEG. C, FLOW 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
4.21	0.00	0.100E-01	0.021	0.117
4.55	54.80	0.985E-02	0.024	0.136
4.88	853.46	0.756E-02	0.027	0.152
5.21	1331.09	0.620E-02	0.029	0.165
5.55	1519.01	0.566E-02	0.031	0.176
5.88	1620.80	0.537E-02	0.033	0.186
6.21	1659.95	0.526E-02	0.035	0.196
6.55	1683.44	0.519E-02	0.036	0.206
17.21	1706.93	0.512E-02	0.091	0.513
18.21	1808.72	0.483E-02	0.096	0.541
19.21	1910.51	0.454E-02	0.101	0.567
20.21	2012.30	0.425E-02	0.106	0.592
21.21	2114.09	0.396E-02	0.110	0.615
22.21	2215.88	0.367E-02	0.113	0.636
23.21	2325.50	0.335E-02	0.117	0.656
24.21	2427.29	0.306E-02	0.120	0.674
25.21	2513.42	0.282E-02	0.123	0.690
26.21	2599.55	0.257E-02	0.126	0.705
27.21	2677.25	0.235E-02	0.128	0.719
28.21	2740.47	0.217E-02	0.131	0.731
29.21	2803.13	0.199E-02	0.133	0.743
30.21	2857.94	0.183E-02	0.135	0.754
31.21	2912.75	0.167E-02	0.136	0.764
32.21	2959.73	0.154E-02	0.138	0.773
33.21	3014.54	0.138E-02	0.139	0.781
34.21	3045.86	0.129E-02	0.141	0.788
35.21	3085.01	0.118E-02	0.142	0.795
36.21	3124.16	0.107E-02	0.143	0.801
37.21	3147.65	0.100E-02	0.144	0.807
38.21	3186.30	0.895E-03	0.145	0.813
39.21	3210.49	0.828E-03	0.146	0.817
40.21	3257.27	0.694E-03	0.147	0.822
47.46	3500.00	0.000E 00	0.179	1.000

The use of a soluble calcium salt to impregnate the fly ash is uneconomical, and methods were sought to impregnate the fly ash with lime in a less costly manner. Because limestone costing about $2/ton can be injected into a furnace directly and used to sorb SO_2 in a competing SO_2 removal process[70], it was obvious that only low-cost techniques for impregnating the fly ash with lime could be considered in these studies.

Calcium hydroxide is too insoluble in water to be impregnated on fly ashes in significant amounts. Fly ash samples impregnated as many as ten times with saturated calcium hydroxide solution sorbed less than 1 weight percent SO_2. Mixing fly ash with concentrated slurries of calcium hydroxide in water followed by drying at temperatures as high as 600°C produced poor SO_2 sorbents.

When impregnated on fly ashes with sodium concentrations of up to 5 weight percent, sodium carbonate solutions gave sorptions that were essentially stoichiometric. Higher concentrations did not give increased sorptive capacity. This was attributed to the fact that the fly ash had such a low surface area that the additional sodium carbonate was merely deposited on the impregnated fly ash in thicker layers and did not react with the SO_2. Sodium carbonate is too expensive to be used in a once-through system. The studies, however, were of help in developing the sodium carbonate sorption concept described below.

In a further effort to obtain superior SO_2 sorbents from calcium hydroxide and/or calcium carbonate and fly ash, the use of a wetting agent was tried. It has been reported that sodium silicate wets fly ash. Therefore, mixtures of calcium hydroxide, sodium silicate and fly ash were prepared by various techniques and tested for SO_2 sorption. The data in Table III shows that mixtures of fly ash, calcium hydroxide and sodium silicate dried at room temperatures for up to two days sorbed 2 weight percent SO_2. Sorption decreased as the drying time was increased or as the drying temperature was increased above 125°C. In the absence of lime, the sodium silicate-impregnated fly ash sorbed less than 0.5 weight percent SO_2.

Another technique commonly used to wet solids is boiling in water. This was tried in preparation R2-28 shown in Table III and the results were roughly the same as those obtained with sodium silicate. Even though wetting of the fly ash gave a marginal improvement, the initial improvement was too low to be of interest.

c. Discussion

Both fly ashes gave weakly alkaline reactions in water and had surface areas of less than 1 m^2/g. Consequently, their poor SO_2-sorbing properties were not unexpected.

The only impregnants which consistently gave good sorption in these studies were strong bases. No way was found to impregnate the fly ashes with the low cost calcium hydroxide or carbonate to make effective SO_2 sorbents. The use of strong bases which are water soluble, such as sodium hydroxide or sodium carbonate, or the preparation of calcium oxide by the decomposition of calcium formate could not be considered for once-through operation because of prohibitively high cost. The amount of money that can be spent impregnating or alkalyzing a fly ash is extremely small, because such materials have to compete with limestone which sells for approximately $2/ton. Thus, there was no economic advantage in further exploration on the use of alkalized fly ash for removal of SO_2.

The concept of using alkaline coal ash or fly ash as an SO_2 sorbent could only be feasible if a source of a very alkaline fly ash were available in extremely large quantities. To explore this possibility, a study was made of the analyses of the ashes of American coals.[30] The anthracite and bituminous coal of the United States have relatively high silica and alumina contents in their ashes, and relatively low metal oxide contents. Thus, the ash of the West Virginia coal which was tested had over 80% combined silica and alumina, only about 2% CaO, and less than 2% Na_2O and K_2O combined. This West Virginia coal ash was typical of the bituminous coals in this country and would not be expected to have SO_2 sorptive properties.

Some of the younger western coals which have as much as 30% calcium oxide in the ash and less than 40% silica and alumina combined probably would have more basic ashes and would be better sorbents for SO_2. However, these ashes are located in areas far removed from large population densities and, in most instances, these younger western coals have so little sulfur that sulfur removal presents almost no problem. Therefore, there would be no incentive or need to use their basic fly ash for removing sulfur. The cost of shipping such fly ashes to other areas would be prohibitively expensive and could not compete with shipment of limestone. Thus, the use of alkalized fly ash for removing sulfur dioxide does not appear to be promising in this country.

2. Slags

Iwamura[33] reported that copper blast furnace slag had good SO_2 sorption properties. Although a study of the translation of this paper cast doubt as to the usefulness of such slags for removing SO_2 from flue gases, two copper slags were obtained from the Kennecott Copper Company and tested. The first, a powdered slag obtained from the reverbatory furnace at El Paso, contained 0.3% copper, 39.3% silica, 5.4% alumina, 43% FeO, 5.6% CaO, 1.2% MgO, 1% sulfur, and 2.7% Fe_2O_3 and gave a slightly alkaline reaction in water. The other material was a lumpy slag obtained from the shaft furnace at South Brunswick, New Jersey. It contained 10% copper and its other major constituents were calcium, magnesium and silica. Neither slag, as seen in Table VI, sorbed more than 1 weight percent SO_2 in screening runs made between 20 and 350°C.

A sample of phosphorous slag from the Pocatello, Idaho plant of the FMC Corporation was also evaluated. This slag which assayed 45.4% silica, 42.9% calcium oxide, and 1.4% P_2O_5 sorbed less than 1 weight percent of SO_2 in a scanning run made between 20 and 350°C.

Basic open hearth slags obtained from the United States Steel Plant at Morrisville, Pennsylvania were also tested. Because of their greater basicity, these were expected to be better sorbents for SO_2 than the other slags tested. However, these slags too sorbed only small amounts of SO_2.

The low capacity of all these slags for SO_2 is attributed to their low basicity. Since good metallurgical processing dictates that the quantity of lime added be not greatly in excess of that required to neutralize the silica, it does not seem likely that such slags would be basic enough to be useful as SO_2 sorbents.

TABLE VI

Sorption of SO_2 on Industrial Wastes

Sample No.	Industrial Wastes	Screening Temp. °C	SO_2 Sorbed Wt. %
R2-14	El Paso Copper Blast Furnace Slag 0.3% Cu, 39.3% SiO_2, 5.4% Al_2O_3, 43% FeO, 5.6% CaO, 1% S, 2.7% Fe_2O_3	22-350	<1
R2-14A	South Brunswick slag - 10% Cu; Major Constituents - Ca, Mg, SiO_2	25-350	<1
R2-7	Phosphorous Slag - FMC Pocatello Works - 45.4% SiO_2, 42.8% CaO, 1.4% P_2O_5	20-350	<1
80	U.S.S. Basic Open Hearth Slag	125	1.0
75	U.S.S. Puffed Basic Open Hearth Slag	125	1.5
	Blast Furnace Slag	125	3.1
	Blast Furnace Slag	400	1.5

D. INORGANIC SALTS

1. Sulfides

a. Introduction

Nickel sulfide was reported to have the ability to sorb SO_2. According to Budelot and Delafosse[34], nickel sulfide chemisorbs SO_2 at temperatures of about 120°C. These authors dealt only with the sorption phenomenon and did little more than point out that chemisorption existed and appears to increase with increasing temperature. Other investigators report that nickel sulfide catalyzes the reduction of SO_2 at higher temperatures. Thus, a potential process based on chemisorption at 120°C and desorption at temperatures above 200°C appeared to be a possibility.

The literature mentioned many nickel sulfide compounds in connection with SO_2 sorption. A Russian article discussing the steady state potentials of nickel sulfide points out that samples containing from 21.1 to 35.4% sulfur showed markedly different chemical micro-structure and surface properties.[35]

Wohler and his associates described the reaction of SO_2 with calcium, iron and zinc sulfides and with ores including pyrites.[36] Because of the similarity in properties, iron sulfides might be expected to react similarily to nickel sulfide. However, a thermodynamic investigation of this reaction showed that iron sulfide reacts with SO_2 only at relatively high temperatures and at higher SO_2 partial pressures than would be obtained in flue gases. Along this line, British patent 726,216[37] reports the formation of Fe_3O_4 and sulfur when a stream of oxygen and SO_2 were passed over ferric sulfide at 900 to 1000°C.

b. Experimental

Purchased samples of barium sulfide, cuprous sulfide, cupric sulfide, ferric sulfide, and pyrites (FeS_2) were screened to determine whether these sulfides would sorb or react with SO_2.

None of the sulfides tested sorbed SO_2 at 150°C. At 450°C, barium sulfide sorbed a trace of SO_2 and iron sulfide sorbed about 1 weight percent of SO_2. At 450°C both the cupric and the cuprous sulfide and pyrites (FeS_2) evolved

SO_2 presumably due to the oxidation of the sulfide. The pyrites also evolved copious amounts of sulfur, presumably due to the reactions

$$FeS_2 \rightarrow FeS + S \qquad (1)$$

$$S + O_2 \rightarrow SO_2 \qquad (2)$$

The sulfide sorbents removed from the reactor after sorption at 450°C were analyzed by x-ray diffraction. The cuprous sulfide residue showed the presence of $CuSO_4$, a $CuS{\cdot}Cu_2S$ salt, and CuO. The cupric sulfide was converted mainly to the $CuS{\cdot}Cu_2S$ salt. The pyrites sample showed only FeS_2. The FeS that was expected on the basis of equation (1) shown above was not detected by the x-ray analysis, presumably because it was masked by the bulk FeS_2.

Two nickel sulfides having the formalae NiS and Ni_3S_2 were prepared by direct fusion of the two elements at 250°C. X-ray analysis showed these to be the principal compounds. The NiS compound sorbed no SO_2 at 200 and 300°C, and only a trace at higher temperatures. The Ni_3S_2 compound evolved SO_2 when heated in a synthetic flue gas sample. The appearance of nickel oxide in the treated samples indicates that the Ni_3S_2 was partially oxidized by the oxygen in the synthetic flue gas sample.

c. Discussion

In the literature cited above on the sorption of SO_2 with sulfides, all work on the reactions of sulfides with SO_2 was done with pure SO_2, and the results obtained were markedly different from those obtained in our work. With synthetic flue gas, sulfides tended to oxidize with the oxygen in the flue gas sample rather than react with the SO_2 that was present in a much lower concentration.

Other inorganic sulfides that might react more favorably with SO_2 in flue gas were considered. Based on thermodynamics, the most promising sulfides were magnesium sulfide, manganese sulfides, and calcium sulfide. Magnesium sulfide is unstable in the presence of moisture and probably would not react well with SO_2 in a synthetic flue gas mixture. Manganese sulfide was eliminated because of the relatively high cost of its preparation. It was also believed that the oxides of magnesium and manganese would be far better sorbents for SO_2 than the sulfides, and these oxides are being studied by others. Calcium sulfide was not of interest since it could not compete economically with limestone processes used to remove SO_2. Consequently, no work was done with these sulfides.

2. Sodium Silicates

a. Introduction

A paper by Takats[38] showed that a significant reaction of SO_2-air mixtures with various silicates occurred below their softening range. Products made by fusing 1, 2, 3, and 4 mols of silica with 2 mols of sodium hydroxide showed SO_2 sorptions of 15 to 20% by weight at elevated temperatures. The most active material prepared by Takats was made by reacting 2 mols of silica with 2 mols of sodium hydroxide. This was not expected, since Takats thought that the reactivity of SO_2 in the gas phase with sodium silicates would increase as the basicity of the silicates increased, and thus the material having a 2 to 1 sodium hydroxide to silica ratio should have had the best SO_2 sorption characteristics.

Takats explained his results by saying that the greater activity of the $2NaOH{:}2SiO_2$ material was due to the greater molecular mobility of the di-silicate which had the lowest melting point,claiming that "although it is not possible to use the melting point of the crystaline substance as a strict measure for the molecular mobility of a glass phase, such a relationship nevertheless should make certain qualitative statements possible". Takats found partial confirmation of his reasoning in a study made on the reactivity of glasses of other alkaline metals. For glasses made with 2 mols of the respective alkalis per mol of silica, the reactivity was of the order of K>Na>Li, which correlates with their respective melting points. Thus, potassium metasilicate melts below 1000°C, lithium at 1200°C and sodium at an intermediate value.

b. Experimental

Sodium silicates were made by dissolving Harshaw crushed silica in concentrated sodium hydroxide solution. The composition, drying temperatures, and yields of the various sorbents are shown in Table VII, which also shows the results obtained when the samples were used to sorb SO_2.

TABLE VII

Sorption of SO_2 From Synthetic Flue Gas on Sodium Silicates Made by Dissolving Silica in Caustic Solutions

Sample No.		Sorption Temp. °C	SO_2 Sorbed Wt. %
T5-6	$2NaOH \cdot SiO_2$ - Dried @ 140°C	21	5
		140	2
		250	Plugged
T5-7	$2NaOH \cdot 1.5SiO_2$ - Dried @ 140°C	21	8
		250	Plugged
T5-8	$2NaOH \cdot 2SiO_2$ - Dried @ 140°C	22	10
		250	Plugged
T5-11	$2NaOH \cdot 2SiO_2$ - Dried @ 200°C	22	7.8
		250	Plugged
T5-12	$2NaOH \cdot 2SiO_2$ - Dried @ 300°C	23	10.3
		250	8.6
T5-13	$2NaOH \cdot 2SiO_2$ - Dried @ 400°C	22	14
		250	7.6
		350	13.5
T5-16	$2NaOH \cdot 2SiO_2$ - Made by Impregnating NaOH on Silica, Dried @ 400°C	250	2.3

To be effective, the silicates had to be dried at a higher temperature than that at which sorption was made. Sorption at 250°C was usually less than that obtained at 25°C. A screening run, sample T5-13, showed more sorption at 350°C than at 250°C; and an additional run at 450°C not shown in the Table, gave a still better sorption of SO_2. This high temperature sorption activity, however, was not pursued as such temperatures were deemed impractical for use in removing SO_2 from stack gases.

For comparison, sample T5-16, a sodium hydroxide impregnated silica which was dried at 400°C, is included in this Table. Although T5-16 had the same sodium hydroxide to silica ratio as T5-13, this impregnated silica was a much inferior SO_2 sorbent.

Despite their relatively high SO_2 sorptions, sodium silicate glasses were not viewed as potential SO_2 sorbents. Regeneration is difficult if not impractical, and the cost of sodium hydroxide would rule out its use in non-regenerative systems. Studies with hydrogen at 600°C and 800°C showed that only 4 and 19% respectively of the sorbed SO_2 could be desorbed. The Philadelphia Quartz Company, marketers of sodium silicates, could offer no advice as to how the SO_2 could be recovered or how the sodium silicate might be regenerated. Therefore, work on this system was abandoned.

c. Discussion

The fact that sorption at 25° and at 350° was higher than at intermediate temperatures of 150 to 250°C, suggests that more than one mechanism is involved in these studies. Sorption at room temperature may have been due to the presence of residual moisture, which would have aided reaction between the sodium hydroxide and the SO_2. Because the samples gained high temperature sorption activity only after being dried at still higher temperatures than those used for the evaluation indicates that the high temperature treatment may have been more than mere drying. The loss of retained moisture on heating may have caused development of greater porosity in the samples which could explain the increase in sorptive capacity of the sodium silicates as drying temperatures were raised. This porosity concept is consistent with the fact that the sample of silica impregnated with a relatively thick layer of sodium hydroxide was a poor sorbent (Run T5-16). Thus, sodium silicate glasses may sorb SO_2 because of their relatively strong basicity, and the formation or development of "porous" surfaces by the heat treatment may be somewhat analogous to the introduction of sodium hydroxide or carbonate on silica gels having a large pore surface. (see below)

3. Sodium Carbonates

Sodium carbonate-impregnated silica gel was shown to be an active SO_2 sorbent in the 125-150°C range (see page 73 below) the range at which flue gas is emitted from power plants. From the power plant's point of view, this generally is the most favorable sorption temperature since treating stack gas as it enters the stack causes the least disruption to normal power plant operation.

In studying impregnated sodium carbonate materials, the Na_2CO_3 supports that gave best sorption were not able to withstand the temperatures required to regenerate the sodium sulfite or sodium sulfate which form when SO_2 and SO_3 are sorbed on sodium carbonate. Active supports must have large surface areas. Thus, fly ash, clays and slags and other low surface area inexpensive materials were ineffective supports for soda ash. The lowest cost, temperature-resistant support believed to have the surface properties and thermal stability required for a regenerable sodium carbonate-impregnated sorbent was activated bauxite which was used as a copper support (see page 118) and which sells for $140/ton. By contrast, sodium carbonate, the active material, sells for $32/ton. If sodium carbonate itself is used as an SO_2 sorbent, the cost and temperature limitations imposed by the support would be eliminated.

Several forms of soda ash were evaluated for their SO_2 sorption properties and these showed a wide range of values, as seen in Table VIII. A sample of Baker CP soda ash sorbed 12.7 weight percent SO_2, the lowest value found. FMC grade 50 Na_2CO_3 is less porous than either the 100 or 120 grade and sorbed less SO_2. Natural ash, which is calcined trona, probably has good sorptive capacity because it is pseudomorphic with trona. Hydrated and dehydrated sesquicarbonates showed SO_2 sorptions of 34.5 and 46 weight percent, showing that $NaHCO_3$ enhanced SO_2 sorption. The increased sorption on drying the sesquicarbonate was somewhat greater than that calculated for loss of moisture from $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$. A sample of sodium bicarbonate sorbed over 48 weight percent of SO_2. Computer sheets showing variations in SO_2 break-

TABLE VIII

Sorption of SO_2 on Sodium Carbonates

Sorbent	Wt. % SO_2 Sorbed	Stoichiometric Sorption, %
Baker CP Grade Na_2CO_3	12.7	21.0
FMC Grade 50 Na_2CO_3	18.2	30.2
FMC Grade 120 Na_2CO_3	20.1	33.3
FMC Grade 100 Na_2CO_3	25.4	42.1
Natural Ash	38.6	64.0
Precipitator Cake (Impure Sesquicarbonate)	33.0	77.8
FMC Sodium Sesquicarbonate	34.5	81.3
FMC Anhydrous Sodium Sesquicarbonate	46.2	91.5
Sodium Bicarbonate	48.1	>100

through and loadings with time for those materials are shown in Tables IX through XV.

These sorptions, the highest found in these studies, prompted a study to develop a regenerative process for using sodium carbonates as SO_2 sorbents. This work is described below.

4. Copper-Impregnated Sorbents

British patent 1,089,716[39] describes a process for removing sulfur dioxide from gas mixtures with a Redox catalyst. As used in this patent, "Redox catalyst" refers to a material "capable of chemically binding sulfur dioxide under oxidative conditions". The patent claims that copper-impregnated catalyst can remove SO_2 from flue gas compositions at temperatures above 300°C and that the catalyst can be regenerated and the sulfur dioxide recovered by treating the spent catalyst with either reducing gas or hydrocarbon gas mixtures at temperatures approximately 50 to 100°C higher than the sorption temperatures used. The patent claims that a wide variety of materials can be used as carriers for the copper. These materials included natural clays, bauxite, silica, silica-alumina, silica-magnesia, and mixtures thereof.

Copper-impregnated sorbents were prepared by impregnating the respective supports with copper nitrate solution and drying with stirring to insure distribution of the copper on the carrier. Two series of products having the copper contents shown in Table XVI were made. In the first, the copper nitrate was impregnated on the carriers and dried at 250°C. In the second, the copper-impregnated materials were dried at 120-140°C and were then reduced with methane or hydrogen at 550°C for 12-16 hours. Samples normally were reduced overnight in order not to tie up equipment during the working day. However, some copper-impregnated materials were activated in as little as 6-8 hours in other studies. Carbon based copper-impregnated materials were dried in inert or reducing atmospheres to prevent oxidation or combustion of the carbon.

Unreduced copper-impregnated materials were relatively poor sorbents for SO_2. The data in Table XVI show that 8% copper on silica and on various clays sorbed less than 1 weight percent SO_2 in screening runs made over the temperature range of 22-350°C. Nuchar carbon was a fairly effective sorbent, particularly at 300°C where 7.5% copper on Nuchar

NOT REPRODUCIBLE

TABLE IX

RUN 58 FMC SODA ASH GRADE 50
ONE GRAM, TEMP 125 DEG. C, FLOW 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME - MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
0.50	117.15	0.119E-02	0.000	0.001
0.66	183.05	0.124E-02	0.000	0.002
0.83	263.59	0.127E-02	0.000	0.003
1.00	424.68	0.107E-02	0.000	0.004
1.16	622.38	0.124E-02	0.001	0.005
1.33	849.37	0.136E-02	0.001	0.007
1.50	1039.74	0.150E-02	0.001	0.008
1.66	1200.83	0.124E-02	0.001	0.009
1.83	1332.63	0.974E-03	0.001	0.010
2.00	1442.46	0.768E-03	0.002	0.011
2.16	1537.65	0.597E-03	0.002	0.012
2.33	1610.87	0.172E-02	0.002	0.013
2.50	1676.77	0.272E-02	0.002	0.015
2.83	1771.96	0.364E-02	0.003	0.021
3.33	1889.12	0.387E-02	0.005	0.031
4.00	1984.30	0.382E-02	0.008	0.045
5.50	2094.14	0.379E-02	0.014	0.077
9.83	2196.65	0.372E-02	0.030	0.166
12.33	2299.16	0.343E-02	0.039	0.215
14.83	2394.35	0.316E-02	0.047	0.260
17.83	2496.86	0.286E-02	0.056	0.310
20.00	2540.79	0.274E-02	0.062	0.344
20.66	2562.76	0.268E-02	0.064	0.353
21.66	2592.05	0.259E-02	0.067	0.368
22.66	2621.33	0.251E-02	0.069	0.382
23.66	2650.62	0.242E-02	0.072	0.396
24.16	2665.27	0.238E-02	0.073	0.402
25.33	2694.56	0.230E-02	0.076	0.417
72.04	3500.00	0.000E 00	0.182	1.000

NOT REPRODUCIBLE

TABLE X

RUN 60 FMC SODA ASH GRADE 120
ONE GRAM, TEMP. 125 DEG. C FLOW1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
0.66	0.00	0.176E-02	0.000	0.002
0.83	153.76	0.158E-02	0.000	0.004
1.00	336.82	0.132E-02	0.001	0.005
1.16	534.51	0.149E-02	0.001	0.006
1.33	585.77	0.212E-02	0.001	0.008
4.66	651.67	0.776E-02	0.018	0.089
6.16	588.28	0.788E-02	0.029	0.148
6.33	842.05	0.745E-02	0.031	0.154
6.50	951.88	0.715E-02	0.032	0.160
7.00	1171.54	0.656E-02	0.035	0.177
7.50	1369.24	0.602E-02	0.038	0.193
8.00	1508.56	0.565E-02	0.041	0.207
9.00	1584.10	0.517E-02	0.047	0.234
10.00	1837.38	0.475E-02	0.052	0.259
11.00	1911.08	0.454E-02	0.056	0.282
12.00	1954.30	0.433E-02	0.061	0.304
13.00	2028.24	0.420E-02	0.065	0.325
16.50	2035.56	0.418E-02	0.080	0.398
18.00	2072.17	0.408E-02	0.086	0.429
20.00	2138.07	0.389E-02	0.094	0.468
22.00	2269.77	0.351E-02	0.101	0.505
23.00	2328.45	0.335E-02	0.105	0.522
24.00	2408.99	0.312E-02	0.108	0.538
25.00	2496.85	0.286E-02	0.111	0.553
26.00	2555.43	0.270E-02	0.114	0.567
27.00	2592.05	0.259E-02	0.117	0.580
28.00	2679.91	0.234E-02	0.119	0.592
29.00	2738.49	0.217E-02	0.121	0.603
45.44	3500.00	0.000E 00	0.201	1.000

TABLE XI

NOT REPRODUCIBLE

RUN 54 FMC SODA ASH GRADE 100
ONE GRAM, TEMP. 125 DEG C 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
2.16	0.00	0.499E-02	0.005	0.021
2.33	100.61	0.604E-02	0.006	0.024
2.50	165.29	0.704E-02	0.007	0.029
3.00	402.46	0.782E-02	0.011	0.043
4.00	718.68	0.744E-02	0.018	0.073
5.00	984.59	0.689E-02	0.025	0.101
6.00	1164.27	0.650E-02	0.032	0.128
7.00	1351.12	0.605E-02	0.038	0.152
8.00	1494.86	0.569E-02	0.044	0.176
9.00	1617.04	0.536E-02	0.050	0.197
10.00	1724.84	0.507E-02	0.055	0.218
11.00	1811.08	0.483E-02	0.060	0.237
12.00	1897.33	0.458E-02	0.065	0.256
13.00	1947.63	0.443E-02	0.069	0.273
14.00	2077.00	0.406E-02	0.074	0.290
15.00	2170.43	0.380E-02	0.077	0.306
16.00	2220.73	0.365E-02	0.081	0.320
17.00	2271.04	0.351E-02	0.085	0.334
18.00	2314.16	0.339E-02	0.088	0.348
19.00	2357.28	0.326E-02	0.092	0.361
20.00	2400.41	0.314E-02	0.095	0.374
21.00	2429.15	0.306E-02	0.098	0.386
22.50	2479.46	0.291E-02	0.102	0.403
24.50	2673.51	0.236E-02	0.108	0.424
26.50	2731.00	0.219E-02	0.112	0.442
29.00	2781.31	0.205E-02	0.117	0.463
31.00	2817.24	0.195E-02	0.122	0.479
33.00	2853.18	0.184E-02	0.125	0.494
34.00	2867.55	0.180E-02	0.127	0.501
37.00	2917.96	0.166E-02	0.132	0.521
39.16	2946.61	0.158E-02	0.136	0.535
41.33	2968.17	0.152E-02	0.139	0.548
43.66	2996.91	0.143E-02	0.143	0.562
*****	3500.00	0.000E 00	0.254	1.000

NOT REPRODUCIBLE

TABLE XII

RUN 57 NA2CO3 PRECIPITATOR CAKE
ONE GRAM, TEMP. 125 DEG. C 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
5.50	0.00	0.978E-02	0.026	0.081
5.66	337.52	0.883E-02	0.028	0.085
6.00	374.21	0.876E-02	0.031	0.095
7.00	491.61	0.851E-02	0.040	0.121
8.00	594.33	0.826E-02	0.048	0.146
9.00	675.05	0.806E-02	0.056	0.171
10.00	755.76	0.784E-02	0.064	0.195
11.00	829.14	0.763E-02	0.072	0.218
12.00	902.51	0.742E-02	0.079	0.241
13.00	990.56	0.717E-02	0.087	0.263
14.00	1093.29	0.688E-02	0.094	0.285
15.00	1188.67	0.660E-02	0.100	0.305
16.00	1298.74	0.629E-02	0.107	0.325
17.00	1401.46	0.600E-02	0.113	0.343
18.00	1504.19	0.570E-02	0.119	0.361
19.00	1606.91	0.541E-02	0.124	0.378
20.00	1709.64	0.512E-02	0.130	0.394
21.00	1805.03	0.484E-02	0.135	0.409
22.00	1885.74	0.461E-02	0.139	0.423
23.00	1973.79	0.436E-02	0.144	0.437
24.00	2047.16	0.415E-02	0.148	0.450
25.00	2120.54	0.394E-02	0.152	0.462
26.00	2186.58	0.375E-02	0.156	0.474
27.00	2252.62	0.356E-02	0.160	0.485
28.00	2311.32	0.339E-02	0.163	0.495
29.00	2362.68	0.325E-02	0.167	0.505
31.00	2458.07	0.297E-02	0.173	0.524
32.00	2502.09	0.285E-02	0.176	0.533
33.00	2538.78	0.274E-02	0.178	0.541
34.00	2568.13	0.266E-02	0.181	0.550
35.16	2612.15	0.253E-02	0.184	0.559
36.00	2641.50	0.245E-02	0.186	0.565
37.00	2670.85	0.237E-02	0.189	0.572
38.00	2700.20	0.228E-02	0.191	0.579
39.00	2722.22	0.222E-02	0.193	0.586
91.23	3500.00	0.000E 00	0.330	1.000

NOT REPRODUCIBLE

TABLE XIII

RUN #3 NATURAL ASH
ONE GRAM, TEMP. 125 DEG. C, 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
2.00	0.00	0.489E-02	0.004	0.012
3.00	264.70	0.822E-02	0.011	0.029
4.00	382.35	0.840E-02	0.019	0.051
5.00	448.52	0.842E-02	0.028	0.072
6.00	492.64	0.842E-02	0.036	0.094
7.00	544.11	0.836E-02	0.045	0.116
8.00	595.58	0.826E-02	0.053	0.137
9.00	639.70	0.816E-02	0.061	0.159
10.00	683.82	0.805E-02	0.069	0.180
11.00	742.64	0.788E-02	0.077	0.200
12.00	794.11	0.773E-02	0.085	0.220
14.00	919.11	0.738E-02	0.100	0.259
15.00	985.29	0.719E-02	0.107	0.278
16.00	1227.94	0.649E-02	0.114	0.296
18.00	1367.64	0.609E-02	0.127	0.328
20.00	1492.64	0.574E-02	0.139	0.359
22.00	1602.94	0.542E-02	0.150	0.388
24.00	1713.23	0.510E-02	0.160	0.415
26.00	1816.17	0.481E-02	0.170	0.441
28.00	1904.41	0.456E-02	0.180	0.465
31.00	2036.76	0.418E-02	0.193	0.499
34.00	2191.17	0.374E-02	0.205	0.530
36.00	2264.70	0.353E-02	0.212	0.549
37.00	2301.47	0.342E-02	0.215	0.558
40.00	2404.41	0.313E-02	0.225	0.583
43.00	2485.29	0.290E-02	0.234	0.606
47.00	2595.58	0.258E-02	0.245	0.635
49.00	2647.05	0.243E-02	0.250	0.648
51.00	2750.00	0.214E-02	0.255	0.660
70.03	3500.00	0.000E 00	0.386	1.000

NOT REPRODUCIBLE

TABLE XIV

RUN 55 FMC SODIUM SESQUICARBONATE
ONE GRAM, TEMP, 125 DEG. C 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
1.50	1371.21	0.654E-03	0.000	0.001
2.00	1522.72	0.538E-03	0.000	0.002
3.00	1643.93	0.427E-02	0.003	0.009
4.50	1712.12	0.470E-02	0.009	0.028
5.00	1727.27	0.477E-02	0.012	0.035
5.50	1734.84	0.482E-02	0.014	0.042
22.00	1742.42	0.502E-02	0.095	0.278
23.16	1795.45	0.487E-02	0.101	0.294
24.16	1833.33	0.476E-02	0.106	0.308
24.50	1856.06	0.470E-02	0.108	0.313
25.00	1878.78	0.463E-02	0.110	0.320
26.00	1924.24	0.450E-02	0.115	0.333
27.00	1969.69	0.437E-02	0.119	0.346
28.00	2022.72	0.422E-02	0.123	0.358
29.00	2068.18	0.409E-02	0.127	0.370
30.00	2106.06	0.398E-02	0.131	0.382
31.00	2159.09	0.383E-02	0.135	0.393
32.00	2196.96	0.372E-02	0.139	0.404
33.00	2234.84	0.361E-02	0.143	0.415
34.00	2280.30	0.348E-02	0.146	0.425
35.00	2318.18	0.337E-02	0.150	0.435
35.50	2378.78	0.320E-02	0.155	0.449
38.00	2431.81	0.305E-02	0.159	0.463
39.00	2469.69	0.294E-02	0.162	0.472
40.00	2507. 7	0.283E-02	0.165	0.480
41.00	2537.87	0.275E-02	0.168	0.488
42.50	2590.90	0.259E-02	0.172	0.500
43.50	2621.21	0.251E-02	0.175	0.507
44.50	2651.51	0.242E-02	0.177	0.514
45.00	2666.66	0.238E-02	0.178	0.518
46.00	2689.39	0.231E-02	0.181	0.525
46.50	2704.54	0.227E-02	0.182	0.528
*****	3500.00	0.000E 00	0.345	1.000

NOT REPRODUCIBLE

TABLE XV

RUN 36 ANHYDROUS SODIUM SESQUICARBONATE
ONE GRAM, TEMP. 125 DEG. C 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
5.00	0.00	0.971E-02	0.024	0.052
6.00	86.95	0.958E-02	0.033	0.073
6.50	137.68	0.948E-02	0.038	0.083
7.00	181.15	0.939E-02	0.043	0.093
8.00	289.85	0.913E-02	0.052	0.113
9.00	398.55	0.885E-02	0.061	0.133
10.00	500.00	0.857E-02	0.070	0.152
11.00	594.20	0.831E-02	0.078	0.170
12.00	688.40	0.804E-02	0.087	0.188
13.00	775.36	0.779E-02	0.094	0.205
14.00	869.56	0.752E-02	0.102	0.221
15.00	949.27	0.729E-02	0.109	0.237
16.00	1021.73	0.708E-02	0.117	0.253
17.00	1108.69	0.683E-02	0.124	0.268
18.00	1231.88	0.648E-02	0.130	0.282
19.00	1311.59	0.625E-02	0.137	0.296
20.00	1384.05	0.605E-02	0.143	0.309
21.00	1456.52	0.584E-02	0.149	0.322
22.00	1514.49	0.567E-02	0.155	0.335
23.00	1579.70	0.549E-02	0.160	0.347
24.00	1637.68	0.532E-02	0.166	0.358
25.00	1688.40	0.518E-02	0.171	0.370
26.00	1739.13	0.503E-02	0.176	0.381
28.00	1833.33	0.476E-02	0.186	0.402
29.00	1876.81	0.464E-02	0.190	0.412
30.00	1920.28	0.451E-02	0.195	0.422
31.00	1956.52	0.441E-02	0.199	0.432
97.13	3500.00	0.000E 00	0.462	1.000

TABLE XVI

Sorption of SO_2 on Copper-Impregnated Materials

Catalyst Number	Description	Sorption Temp. °C	SO_2 Sorbed Wt. %
	Copper-Impregnated Materials Dried @ 250°C		
T21-1	7.6% Cu on Silica	22-350	<1
T21-3A	8% Cu on Montmorillonite	22-350	<1
T21-3B	8% Cu on Metabentonite	22-350	<1
T21-4A	7.4% Cu on Kaolinite	22-350	<1
T21-5B	7.5% Cu on Nuchar Carbon	200 300	3 6.5
T21-6	8% Cu on Alumina	22-350	2-3
T21-7	8% Cu on Silica-Alumina	22-350	2-3
T21-2A	7.5% Cu on 3-8 Mesh SiO_2 Gel	150	4
T21-2B	7.3% Cu on 100-200 Mesh SiO_2 Gel	150	4.5
	Copper-Impregnated Materials Reduced With Methane @ 550°C for 16 Hours		
T21-11	17.8% Cu on S-46 Houdry Silica-Alumina	350	16
T21-15	11.3% Cu on S-46 Houdry Silica-Alumina	400	18.4
T21-13	6.6% Cu on S-46 Houdry Silica-Alumina	400	8.4
T21-14	3.9% Cu on S-46 Houdry Silica-Alumina	400	6.9
T21-8	27.8% Cu on BPL Carbon	300 375	<1 6
T21-9	17.3% Cu on Silica	22-350	<1
T21-10	16.2% Cu on 100-200 Mesh SiO_2 Gel	22-350	<1

sorbent samples sorbed 6.5 weight percent SO_2. Since Nuchar itself sorbed 6 to 8 weight percent SO_2, the presence of the copper did not enhance the sorptive activity of the carbon. About 4 weight percent SO_2 was sorbed on copper-impregnated silica gels.

Much greater SO_2 sorption resulted when the copper-impregnated silica-alumina was reduced with methane for 16 hours. Thus, sample T21-11 sorbed over 16 weight percent SO_2. A comparison of this result with those for T21-13 and T21-14 shows how SO_2 sorption dropped as the copper content of the sorbent was decreased. However, 11% copper was as effective as 18% (compare T21-11 and 15). The computer calculations for Runs T21-13, 14, 15 are shown in Tables XVII, XVIII, and XIX.

The silica and carbon impregnated materials did not sorb more SO_2 after reduction overnight than when merely dried at 240°C. The reduced copper-impregnated silica gel was a poor sorbent because its structure was destroyed during the long reduction period at 550°C.

Next to the sodium carbonates, the reduced copper-impregnated silica-aluminas were the most active SO_2 sorbents found in these sorption screening studies. These materials too were evaluated for suitability in potential SO_2-removal systems, as described on pages 114 - 126.

5. Molecular Sieves

Several samples of molecular sieves were evaluated for their ability to sorb SO_2. The sieves were supplied by the Davison and Norton Companies and their description is shown in Table XX. A sample of 13 Angstrom Davison sieve with sodium cation sorbed 6 to 7 weight percent of SO_2 at 125°C. A 4 Angstrom Davison sieve with a potassium cation sorbed less than 1 weight percent SO_2 at the same temperature. The higher sorptive capacity of the sodium cation sieve was probably due to the larger pore size of the sieve rather than to any major difference in the basicity of the cation.

The sieves obtained from the Norton Company had openings of from 6 to 9 Angstroms and contained hydrogen, copper, and nickel cations. All were very poor SO_2 sorbents, sorbing less than 2 weight percent SO_2 at 125°C.

TABLE XVII

NOT REPRODUCIBLE

RUN 63 SORBENT T21-15 (11.3 COPPER ON SILICA-ALUMINA)
ONE GRAM, TEMP.400 DEG. C, FLOW 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
1.78	0.00	0.100E-01	0.008	0.048
1.95	94.59	0.973E-02	0.010	0.057
2.11	152.90	0.957E-02	0.012	0.065
2.28	225.57	0.936E-02	0.013	0.074
2.45	305.61	0.913E-02	0.015	0.082
2.61	385.65	0.890E-02	0.016	0.090
3.11	611.22	0.826E-02	0.021	0.114
3.61	793.13	0.774E-02	0.025	0.135
4.11	945.94	0.730E-02	0.028	0.156
4.61	1069.64	0.695E-02	0.032	0.175
5.11	1178.79	0.663E-02	0.035	0.193
5.61	1273.39	0.636E-02	0.039	0.211
6.11	1360.70	0.611E-02	0.042	0.228
6.61	1433.47	0.590E-02	0.045	0.244
7.11	1506.23	0.570E-02	0.048	0.260
7.61	1579.00	0.549E-02	0.050	0.275
8.11	1644.49	0.530E-02	0.053	0.290
8.61	1702.70	0.513E-02	0.056	0.304
9.11	1775.46	0.493E-02	0.058	0.317
9.61	1826.40	0.478E-02	0.061	0.331
10.11	1884.61	0.461E-02	0.063	0.343
10.61	1935.55	0.447E-02	0.065	0.356
11.61	2030.14	0.420E-02	0.070	0.379
12.61	2110.18	0.397E-02	0.074	0.401
13.61	2182.95	0.376E-02	0.078	0.422
14.61	2255.71	0.355E-02	0.081	0.442
15.61	2321.20	0.337E-02	0.085	0.461
16.61	2357.58	0.326E-02	0.088	0.479
17.61	2430.35	0.305E-02	0.091	0.496
18.61	2481.28	0.291E-02	0.094	0.512
19.61	2554.05	0.270E-02	0.097	0.527
20.61	2612.26	0.253E-02	0.100	0.542
21.61	2663.20	0.239E-02	0.102	0.555
22.61	2692.30	0.230E-02	0.104	0.568
49.80	3500.00	0.000E 00	0.184	1.000

NOT REPRODUCIBLE

TABLE XVIII

RUN 30 SORBENT T21-13 (6.6 CU ON SILICA ALUMINA)
ONE GRAM, TEMP. 400 DEG C 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
0.21	0.00	0.000E 00	0.000	0.000
3.55	31.67	0.991E-02	0.016	0.196
3.88	570.13	0.837E-02	0.019	0.232
4.21	934.38	0.733E-02	0.022	0.263
4.55	1187.78	0.661E-02	0.024	0.291
4.88	1377.82	0.606E-02	0.026	0.316
5.21	1520.36	0.566E-02	0.028	0.339
5.55	1639.14	0.532E-02	0.030	0.361
5.88	1726.24	0.507E-02	0.032	0.381
6.21	1805.42	0.484E-02	0.033	0.401
7.21	1995.47	0.430E-02	0.038	0.455
8.21	2153.84	0.384E-02	0.042	0.503
9.21	2288.46	0.346E-02	0.046	0.547
10.21	2415.15	0.310E-02	0.049	0.586
11.21	2510.18	0.283E-02	0.052	0.621
12.21	2605.20	0.255E-02	0.055	0.653
13.21	2692.30	0.230E-02	0.057	0.682
14.21	2779.41	0.206E-02	0.059	0.708
15.21	2874.43	0.178E-02	0.061	0.731
16.21	2937.78	0.160E-02	0.063	0.751
17.21	3016.96	0.138E-02	0.064	0.769
22.54	3111.99	0.110E-02	0.071	0.847
23.21	3135.74	0.104E-02	0.072	0.856
25.21	3183.25	0.905E-03	0.074	0.879
27.21	3230.76	0.769E-03	0.075	0.899
30.21	3294.11	0.588E-03	0.077	0.923
32.21	3325.79	0.498E-03	0.078	0.936
33.21	3341.62	0.452E-03	0.079	0.942
36.21	3373.30	0.362E-03	0.080	0.956
37.21	3397.05	0.294E-03	0.080	0.960
37.88	3404.97	0.271E-03	0.081	0.962
39.88	3468.32	0.905E-04	0.081	0.967
40.21	3476.24	0.679E-04	0.081	0.967
40.27	3500.00	0.000E 00	0.084	1.000

NOT REPRODUCIBLE

TABLE XIX

RUN 31 SORBENT T21-14(3.9 CU ON SILICA ALUMINA)
ONE GRAM, TEMP. 400 DEG. C, 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
2.66	0.00	0.100E-01	0.013	0.190
3.00	816.93	0.767E-02	0.016	0.233
3.33	1609.83	0.540E-02	0.018	0.264
3.66	2058.35	0.412E-02	0.020	0.286
4.00	2290.61	0.345E-02	0.021	0.305
5.00	2594.96	0.258E-02	0.024	0.348
6.00	2739.15	0.217E-02	0.026	0.382
7.00	2835.24	0.190E-02	0.028	0.411
8.00	2915.33	0.167E-02	0.030	0.437
9.00	2995.42	0.144E-02	0.032	0.459
10.00	3051.49	0.128E-02	0.033	0.479
11.00	3107.55	0.112E-02	0.034	0.496
12.00	3147.59	0.100E-02	0.035	0.511
13.00	3179.63	0.916E-03	0.036	0.525
14.00	3219.67	0.801E-03	0.037	0.537
15.00	3251.71	0.710E-03	0.039	0.559
19.00	3283.75	0.619E-03	0.041	0.587
21.00	3291.76	0.595E-03	0.042	0.605
24.00	3299.77	0.572E-03	0.044	0.630
28.00	3315.78	0.526E-03	0.046	0.661
30.33	3323.79	0.503E-03	0.047	0.678
31.99	3331.80	0.481E-03	0.048	0.690
33.33	3339.81	0.458E-03	0.048	0.699
59.74	3500.00	0.000E 00	0.069	1.000

TABLE XX

Sorption of SO_2 on Molecular Sieves

Sample No.	Material	Screening Temp. °C	SO_2 Sorbed Wt. %
	Molecular (Metal Aluminosilicates) Sieves		
R4-16	Davison Grades 564-4A° Pores - K Cation	125	1
R4-17	Davison Grade 544-13A° Pores - Na Cation	125	6
R4-17	Davison Grade 544-13A° Pores - Na Cation	125	7
R4-18	Norton Zeolite - H Cation (7-9AP)	125	1-2
R4-19	Norton Zeolite - Cu Cation (6-7A°)	125	1-2
R4-20	Norton Zeolite - Ni Cation (6-7A°)	125	1-2

NOT REPRODUCIBLE

TABLE XXI

RUN OF SORBENT-13A° MOLECULAR SIEVE -30+100MESH
ONE GRAM, TEMP.125 DEG. C FLOW 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
2.31	42.94	0.598E-02	0.006	0.109
4.64	85.[illegible]8	0.938E-02	0.024	0.391
4.98	214.72	0.909E-02	0.027	0.440
5.31	436.60	0.850E-02	0.030	0.486
5.64	730.06	0.771E-02	0.033	0.528
5.98	1044.93	0.684E-02	0.036	0.567
6.31	1316.97	0.609E-02	0.038	0.601
6.64	1538.85	0.548E-02	0.040	0.631
6.98	1732.10	0.496E-02	0.041	0.659
7.31	1903.88	0.448E-02	0.043	0.684
7.98	2190.10	0.370E-02	0.046	0.727
8.31	2297.54	0.340E-02	0.047	0.745
8.64	2383.43	0.316E-02	0.048	0.762
8.98	2519.42	0.278E-02	0.049	0.778
9.31	2719.93	0.222E-02	0.050	0.791
9.64	2834.35	0.190E-02	0.050	0.802
9.98	2898.77	0.171E-02	0.051	0.812
10.31	2948.[illegible]7	0.157E-02	0.052	0.820
11.31	3056.23	0.126E-02	0.053	0.843
12.31	3142.12	0.102E-02	0.054	0.861
13.31	3206.54	0.839E-03	0.055	0.876
14.31	3256.64	0.695E-03	0.056	0.888
15.31	3299.59	0.573E-03	0.056	0.898
15.64	3313.90	0.532E-03	0.057	0.901
16.31	3335.37	0.470E-03	0.057	0.906
16.64	3342.53	0.450E-03	0.057	0.908
17.64	3399.79	0.286E-03	0.058	0.914
20.06	3500.00	0.000E 00	0.063	1.000

Molecular sieves are fairly expensive materials. Because they are made in batch-type processes, their price could not be expected to drop appreciably below the $1.40/lb price which was quoted. This price in itself did not rule out the use of the sodium cation sieve for SO_2 sorption, because many sorption-desorption reactions with molecular sieves can be carried out for long periods of time with little deterioration of sieve activity. Sieves used for the removal of moisture from gases, removal of acidic gases, and the removal of saturated hydrocarbons from hydrocarbon mixtures have been used in processes which operate many hundred of cycles with little apparent loss of activity in the sieve. An SO_2 sorption-desorption process operating in a similar fashion might be economically feasible.

To test this concept, regeneration of the sodium cation molecular sieve was studied and it was found that regeneration by thermal means was impossible. After prolonged heating at 550°C, the maximum temperature at which the sieve could be heated without destroying its structure, less than 20% of the sorbed SO_2 was removed from the sieve; and on subsequent cycles the sieves sorbed only 1-2 weight percent SO_2. This indicated that the sorption of SO_2 by the Davison sieve was not a true physical sorption but was a reaction between the SO_2 and the sodium cation in the sieve.

Since the only cation which would be expected to sorb SO_2 reversibly was hydrogen, fresh samples of hydrogen cation sieves were obtained from the Norton Company, which claimed that their mordenitic (high silica) Zeolon could sorb 8-10 weight percent SO_2 at temperatures as low as 150°F. The hydrogen cation sieves sorbed virtually no SO_2 at 125°C, but did sorb approximately 4 weight percent SO_2 at room temperature. The low sorptive capacity of the sieve for SO_2 at 125°C was probably due to the fact that this temperature was close to the critical temperature of sulfur dioxide (157.5°C). True physical sorptions only occur when the sorbate can be liquified on the surface of the sorbent and this does not occur at or near the critical temperature.

To test this hypothesis the Zeolon H-cation sieve was run with a synthetic flue gas mixture at 23°C. As shown in Table XXII the sieve sorbed about 4 weight percent of SO_2 at room temperature. Desorption was incomplete at 150°C, as shown in run #85, but was completed and the sieve regained its full capacity when it was regenerated at 200°C, which is well above the critical temperature of SO_2. Several samples of sieves were run through 4 to 5 cycles of sorption at room temperature (23-25°C) and desorption at 200°C with no apparent loss of activity. In a single run made at an intermediate temperature of 80°C, the sieve sorbed only 1 weight percent SO_2.

TABLE XXII

Sorption of SO_2 on Norton H-Cation Sieve

Run No.		Adsorption Temp. °C	SO_2 Sorbed Wt. %
84	Fresh Sieve	23	3.9
85	Sieve after Regeneration at 150°C	23	1.6
83	Fresh Sieve	24	4.1
83A	Sieve after desorption at 200°C	23	3.9
83B	Sieve after second desorption at 200°C	23	4.0
83E	Sieve after fourth desorption at 200°C	23	4.0
81	Fresh Sieve	125	0.5
82	Sieve from Run 81, regenerated at 200°C	23	4.3

These Zeolon H-cation sieves were the only materials found in this study that sorbed SO_2 reversibly. Although the quantity of SO_2 sorbed is not large, and the temperature at which significant sorption occurs is too low to be of interest for flue gas cleanup, this type of SO_2 sorption might be of interest in laboratory studies or cleanup procedures where the relative high cost of the sieve would be of little consequence.

More important, the study showed the hopelessness of obtaining materials that would sorb SO_2 physically at or near its critical temperature. All materials that sorbed significant amounts of SO_2 at or above 125°C reacted with the SO_2 via chemisorption reactions. For this reason, stronger bases made the best sorbents. Unfortunately, the energy that must be expended to reverse the reaction between SO_2 and the strong base is relatively large so that a penalty must be paid for ease of sorption in the overall chemisorption-desorption cycle.

Davison 544 sieve was impregnated with alkalized vanadia by impregnating the sieve with an alkaline solution of ammonium metavanadate, drying at 140°C to remove moisture, and then heating to 560°C in an oxygen atmosphere over a four hour period. The product, which contained 13.9% vanadium and 6.6% sodium, sorbed 12.0 and 10.1% SO_2 at 300°C and 125°C, respectively. (See Tables XXIII and XXIV). This was not an example of the vanadia oxidizing the SO_2 to SO_3 which reacted with moisture and was stored in the sieve openings as H_2SO_4, since SO_2 removal was not achieved by heating to 450°C.

Because of the sieves' high cost, this approach was not studied further.

6. Miscellaneous Salts

Several investigators studied the sorption of SO_2 with barium salts over a temperature range of 100 to 400°C.[40,41,42,43] A screening run made with barium chromate in the temperature range of 25 to 350°C showed it to be a poor SO_2 sorbent. (See Table XXV)

TABLE XXV

Sorption of SO_2 on Miscellaneous Inorganic Salts

Sample No.		Temp. °C	SO_2 Sorbed Wt. %
R4-7	Barium Chromate, 54.4% Ba	25-350	2.0
	Houdry S-46 Silica-Alumina	25-350	1
66	Potassium Carbonate (Allied Chemical)	125	4.8
67	Calcium Carbonate (Fisher)	125	1.9
67A	Calcium Oxide (Fisher)	125	3.5

NOT REPRODUCIBLE

TABLE XXIII

RUN 45 SORBENT R4-21 ALKALIZED VANADIA ON Molecular Sieves
ONE GRAM, TEMP. 300 DEG. C, FLOW 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
0.81	0.00	0.000E 00	0.000	0.000
1.31	587.30	0.698E-02	0.001	0.014
1.48	817.46	0.743E-02	0.002	0.024
1.65	992.06	0.717E-02	0.004	0.034
1.81	1134.92	0.676E-02	0.005	0.044
1.98	1261.90	0.640E-02	0.006	0.053
2.15	1365.07	0.610E-02	0.007	0.062
2.65	1603.17	0.542E-02	0.010	0.086
3.15	1777.77	0.492E-02	0.012	0.107
3.65	1904.76	0.456E-02	0.015	0.127
4.15	2015.87	0.424E-02	0.017	0.145
4.65	2095.23	0.401E-02	0.019	0.162
5.15	2174.60	0.379E-02	0.021	0.179
6.15	2293.65	0.344E-02	0.025	0.209
7.15	2388.88	0.317E-02	0.028	0.236
8.15	2476.19	0.292E-02	0.031	0.262
9.15	2539.68	0.274E-02	0.034	0.285
10.15	2603.17	0.256E-02	0.037	0.307
11.15	2650.79	0.242E-02	0.039	0.328
12.15	2698.41	0.229E-02	0.041	0.348
13.15	2738.09	0.217E-02	0.044	0.366
14.15	2785.71	0.204E-02	0.046	0.384
15.15	2825.39	0.192E-02	0.048	0.400
16.15	2849.20	0.186E-02	0.050	0.416
18.15	2904.76	0.170E-02	0.053	0.445
19.15	2936.50	0.161E-02	0.055	0.459
20.15	2960.31	0.154E-02	0.056	0.472
21.15	2976.19	0.149E-02	0.058	0.485
22.31	3000.00	0.142E-02	0.060	0.499
23.31	3023.80	0.136E-02	0.061	0.511
28.31	3095.23	0.115E-02	0.067	0.563
30.15	3126.98	0.106E-02	0.069	0.580
67.92	3500.00	0.000E 00	0.120	1.000

NOT REPRODUCIBLE

TABLE XXIV

RUN 46 SORBENT R4-21 ALKALIZED VANAIA ON Molecular Sieves
ONE GRAM, TEMP. 125 DEG. C FLOW 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
0.66	0.00	0.176E-02	0.000	0.005
1.00	380.78	0.119E-02	0.001	0.010
1.33	891.20	0.124E-02	0.001	0.014
1.66	1239.58	0.113E-02	0.001	0.018
2.00	1474.53	0.676E-03	0.002	0.021
2.33	1652.77	0.160E-02	0.002	0.025
2.66	1790.50	0.312E-02	0.003	0.032
3.00	1903.93	0.353E-02	0.004	0.044
4.00	2155.09	0.333E-02	0.007	0.077
5.00	2309.02	0.310E-02	0.011	0.109
6.00	2430.55	0.288E-02	0.014	0.138
7.00	2527.77	0.268E-02	0.016	0.166
8.00	2592.59	0.255E-02	0.019	0.192
9.00	2657.40	0.239E-02	0.022	0.216
10.00	2714.12	0.224E-02	0.024	0.239
11.00	2762.73	0.210E-02	0.026	0.260
12.00	2811.34	0.196E-02	0.028	0.280
14.00	2876.15	0.178E-02	0.032	0.317
15.00	2900.46	0.171E-02	0.034	0.334
16.00	2932.87	0.162E-02	0.035	0.351
18.00	2973.37	0.150E-02	0.038	0.381
19.00	2997.66	0.143E-02	0.040	0.396
22.00	3054.39	0.127E-02	0.044	0.436
25.00	3103.00	0.113E-02	0.048	0.471
27.00	3135.41	0.104E-02	0.050	0.493
29.00	3143.51	0.101E-02	0.052	0.513
30.00	3167.82	0.949E-03	0.053	0.523
32.00	3184.02	0.903E-03	0.055	0.541
76.14	3500.00	0.000E 00	0.101	1.000

Houdry S-46 silica-alumina was evaluated since it was used as the support for many copper-impregnated preparations evaluated in this study. The silica-alumina itself sorbed less than 1 weight percent SO_2 in a temperature scanning run.

Potassium carbonate, calcium carbonate and calcium oxide were evaluated to compare their sorptivities with those found for sodium carbonate. Whereas sodium carbonate sorbed 20 to 50 weight percent SO_2, potassium carbonate sorbed only 5 weight percent SO_2 (Table XXVI), and the calcium carbonate even less. The potassium and calcium salts were reagents taken off the shelf and were not prepared in any special form, nor were high surface area materials sought.

E. METALS

A purchased reduced nickel powder was tested for its ability to sorb SO_2. Although the cost of nickel would probably make its use as an SO_2 sorbent uneconomical, it was evaluated to test the proposed system outlined in the following equations:

$$7\mathrm{Ni} + 2\mathrm{SO_2} \rightarrow \mathrm{Ni_3S_2} + 4\mathrm{NiO} \qquad (1)$$

$$\mathrm{Ni_3S_2} + 4\mathrm{NiO} + 6\mathrm{H_2} \rightarrow 7\mathrm{Ni} + 2\mathrm{H_2S} + 4\mathrm{H_2O} \qquad (2)$$

Equation (2) would present no problem as the reaction of both nickel sulfide and nickel oxide with hydrogen proceeds well. The reaction of nickel with SO_2 to form nickel sulfide and nickel oxide was reported by Boudelot and Delafosse.[34] The nickel powder, however, sorbed only traces of SO_2. X-rays showed that much nickel had been converted to the oxide. Apparently the nickel oxidizes with oxygen and/or moisture in flue gas rather than reacting with SO_2 to form the sulfide.

F. COVALENT COMPOUNDS

Two samples of catalyst grade silica carbide received from the Carborundum Company were tested for SO_2 sorption. Both samples had surface areas of less than 1 m^2/g and both sorbed only traces of SO_2.

NOT REPRODUCIBLE

TABLE XXVI

RUN 66 SORBENT ALLIED K2CO3
ONE GRAM, TEMP. 125 DEG. C, FLOW 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
0.16	0.00	0.000E 00	0.000	0.000
0.33	65.71	0.107E-02	0.000	0.001
0.50	108.69	0.121E-02	0.000	0.005
0.83	130.43	0.165E-02	0.000	0.015
1.00	137.68	0.189E-02	0.001	0.021
1.50	166.66	0.409E-02	0.002	0.052
2.00	311.59	0.400E-02	0.004	0.093
2.50	659.42	0.563E-02	0.006	0.143
2.83	978.26	0.591E-02	0.008	0.182
3.00	1130.43	0.574E-02	0.009	0.202
3.16	1260.86	0.554E-02	0.010	0.221
3.50	1478.26	0.512E-02	0.012	0.258
4.00	1746.37	0.450E-02	0.015	0.307
4.50	1956.52	0.400E-02	0.017	0.351
5.00	2130.43	0.361E-02	0.019	0.390
5.50	2282.60	0.325E-02	0.020	0.425
6.00	2405.79	0.295E-02	0.022	0.457
6.33	2442.75	0.273E-02	0.023	0.476
6.66	2557.97	0.257E-02	0.024	0.494
7.00	2630.43	0.239E-02	0.024	0.511
7.33	2688.40	0.224E-02	0.025	0.527
7.66	2731.88	0.213E-02	0.026	0.542
8.00	2775.36	0.203E-02	0.027	0.556
8.33	2840.57	0.185E-02	0.027	0.570
14.74	3500.00	0.000E 00	0.048	1.000

G. NON-METALLIC ELEMENT

The only non-metallic element known to sorb SO_2 in significant amounts is carbon. Because several carbon sorption systems have been studied in considerable detail, no SO_2 sorption studies were made with carbon. However, the desorption of SO_3 and/or H_2SO_4 was studied in several ways, as discussed on pages 80-102 below.

H. OXIDES OF NON-METALS

1. Introduction

Carbon owes its sorptive capacity to its ability to catalyze the oxidation of SO_2 to SO_3 and to store the sulfuric acid that forms by reaction of SO_3 with water in its highly porous structure. Silica gel, an oxide of a non-metal which was reported to sorb SO_3[44], also has a highly porous matrix and, unlike carbon, is inert to sulfuric acid. Thus, sulfuric acid stored in the pores of the silica gel would not react with the gel on thermal desorption, as is the case when sulfuric acid is sorbed on carbon. These facts suggested the possibility of making "a synthetic carbon" by using impregnated silica gels in which the impregnant would oxidize the SO_2 to SO_3. By adding to the gel minor components which are catalytic for the oxidation of SO_2, it was hoped that it would be possible to prepare an adsorbent which functions like carbon but which is resistant to H_2SO_4. The oxidation catalyst could be incorporated into the gel either by conventional impregnation procedures or by co-precipitation with the gel.

An extensive literature survey on the sorptive properties of silica gel and of impregnated silica gels for SO_2 is presented in the Phase I report of this project.[44] Silica gel sorbs SO_2 reversibly. Adsorption of SO_2 is aided by increased surface area of the gel. Silica gel sorbs water as well as SO_2, and this might be a competing reaction in trying to sorb SO_2 from flue gas. However, silica gels which show the optimum capacity for sorbing SO_2 usually contain a minimum of about 5% of adsorbed water, and since this is the approximate water content of flue gases, the presence of such concentrations of water probably would not affect the ability of gels to sorb SO_2.

Although the evaluation of the literature in the Phase I report mentioned above indicated that silica gel per se probably would not be a good sorbent for SO_2 in concentrations found in flue gases, many references claimed that "doped" silica gels adsorb fairly large concentrations of SO_2. The best promoters or impregnants reported in the literature were sodium, iron, tin, chromium, platinum, vanadium, and barium-vanadium compound. The ability of doped silica gels to remove SO_2 and SO_3 from gas streams is apparently a function of gel porosity. Many references dealt with the properties of vanadium-impregnated silica gels used to promote the oxidation of SO_2 to SO_3 for the manufacture of sulfuric acid. Thus, there was much support for the concept of developing an impregnated or co-precipitated silica gel which would have the capacity to oxidize SO_2 to SO_3 which could then be stored in the silica gel.

2. Experimental

a. Preparation of Silica Gel

Silica gels were prepared by the method outlined by Inorganic Synthesis[45]. In this preparation, 100 cc of Fisher sodium silicate solution was diluted with 500 cc of distilled water and an acid solution consisting of 66 cc of sulfuric acid and 100 cc of distilled water was prepared. The two solutions were mixed rapidly with efficient stirring and allowed to stand overnight. Using these proportions, gelling started almost at once and a firm gel formed after standing for at least 12 hours.

After being forced through a 12-mesh screen into a Pyrex tray, the gel was covered with distilled water and allowed to stand for a minimum of 30 minutes. The gel was washed at least eight times by decanting the wash water through a Buchner funnel and the gel was then dried in an evaporating dish at 140°C. The gel caked on drying and was crushed to the desired size fraction.

Gels were impregnated in one of two ways. Some gels were allowed to soak up a specific quantity of a salt solution. The soaking capacity of gel was determined, and that quantity of solution which would be soaked up by the gel and would give even distribution of the metal ion over the surface of the gel was used to impregnate the gel. Other gels were made by dissolving metal salts to be impregnated in the sulfuric acid that was used for the acidification. This technique was practical for sulfates of compounds that were soluble in water and also insured even distribution of the metal throughout the gel.

Two silica gels having the properties shown below were obtained from Davison Chemical Division of Grace Company.

TABLE XXVII

Physical Properties of Davison Silica Gels

Grade	03	59
Mesh Size	3-8	3-8
Surface Area, m^2/g	750-800	340
Pore Volume, cc/g	0.43	1.15
Bulk Density, #/cu. ft.	45	25
g/cc	0.72	0.40

Studies with Na_2CO_3-impregnated silica gels showed that there were no differences in SO_2 sorption capacity between sorbents impregnated on these gels and those made in the lab. To insure uniformity in gel composition and to take advantage of its larger surface area, impregnated samples were made routinely on the 03 gel.

b. Sorption Data

Both Davison gels and all those made in the lab sorbed less than one weight percent SO_2. However, Davison 03 gel sorbed over 100 weight percent of SO_3. This was determined as follows:

> Six-tenths liters of air per minute was bubbled through concentrated sulfuric acid heated to 230°C for six hours, and the air was then passed through a 10 gram column of the Davison 03 silica gel heated at 180-200°C. Concentrated (95%) sulfuric acid has a vapor pressure of 13.4 mm at 235°C,

(Chemical Engineers' Handbook)[46], so that 16.7 grams of sulfuric acid should have been vaporized. Since less than 0.1 gram was collected in a caustic scrubber placed in line after the silica gel, 16.6 grams of sulfuric acid should have been retained by the gel.

Partial desorption of the acid was obtained by passing air through the gel and raising its temperature. Almost no desorption of acid occurred at 350°C, but 5.8 grams were desorbed in five hours at 375-400°C and were trapped in standardized caustic. A considerable amount of untrapped SO_3 fog was also evolved. Titration of an aqueous solution of the cooled gel with base showed that an additional 4-6% sulfuric acid had been retained in the gel.

Table XXVIII shows data for silica gel-based sorbents in which the metal was incorporated in the gel structure by co-precipitation. Silica gels impregnated in this manner with chromium, cobalt, copper, iron, nickel, ammonium metavanadate and barium nitrate were all ineffective sorbents. The amount of SO_2 sorbed in all cases was not more than 1%, which was the amount sorbed by the silica gel itself.

Table XXIX presents data for the sorption of SO_2 on metal-impregnated Davison 03 gel. Silica gels impregnated with barium, chromium, vanadia and vanadia plus sodium hydroxide were ineffective SO_2 sorbents. Vanadia plus sodium hydroxide is reported to be an active catalyst for oxidizing SO_2 to SO_3 in the manufacture of sulfuric acid, but at the temperature range used in this evaluation, it oxidized little if any SO_2.

Samples of calcium formate were impregnated on silica gels. Samples containing 4-8% Ca that had been dried at 140°C showed no sorptive capacity for SO_2. However, a sample with 4-5% Ca that had been dried at 300°C sorbed approximately 2 weight percent SO_2. This gain in sorptive capacity probably was due to some decomposition of calcium formate at the higher drying temperature. To explore this further, calcium nitrate was impregnated on silica gels. After drying at 300°C, a sample containing 2.6% Ca sorbed six weight percent of SO_2 at 200°C. This increased sorption

TABLE XXVIII

Sorption of SO_2 on Coprecipitated Silica Gels
(Metal Salts Dissolved in H_2SO_4 Used to Precipitate Silica Gel)

Sample No.	Impregnant	Maximum Drying Temp. °C	Theoretical Metal Content	Sorption Temp. °C	SO_2 Sorbed Wt. %
T14D-9	Chromium Nitrate	560	2.7% Cr	24 150	<1 <1
T14D-10	Cobaltous Nitrate	140	4.7% Co	100	1
T14D-11	Cobaltous Nitrate	560	2.4% Co	25-300	<1
T14D-12A	Copper Nitrate	140	2.7% Cu	25-300	<1
T14D-12B	Copper Nitrate	560	5.6% Cu	25-300	<1
T14D-13A	Ferric Chloride	140	4.2% Fe	20-300	<1
T14D-13B	Ferric Chloride	600	6% Fe	20-300	<1
T14D-22	Nickelous Acetate	140	3.2% Ni		
T14D-14	Nickelous Acetate	560	2.7% Ni	20-300	Trace
T14D-15	Ammonium Metavanadate	560	19.6% V	20-300	<1
T14D-18	Barium Nitrate	560	10% Ba	26-300	1

TABLE XXIX

Sorption of SO_2 on Impregnated Davison 03 Silica Gels

Sample No.	Impregnant	Maximum Drying Temp. °C	Theoretical Metal Content	Sorption Temp. °C	SO_2 Sorbed Wt. %
T14D-7	Barium Nitrate	140	12.6% Ba	24 150	<1 <1
T14D-8	Chromium Nitrate	140	5.2% Cr	24 150	<1 Trace
T14D-16	Ammonium Vanadate Plus NaOH	560	17.1% V, 8.1% Na	20-300	1
T14D-20	$(Na_4)_2V_2O_4$ + NaOH	560	9.9% V, 5.6% Na	28-300	<1
T14D-17	Ammonium Metavanadate	560	14.7% V	21-300	1
T14D-19A	Calcium Formate	140	4.4% Ca	26-399	Trace
T14D-19E	Calcium Formate	140	8.7% Ca	26-300	Trace
T14D-19C	Calcium Formate	300	4.5% Ca	26-300	2
T14D-19B	Calcium Nitrate	140	2.5% Ca	200 300	2 3
T14D-19D	Calcium Nitrate	300	2.6% Ca	200 300	6 3
T14D-37	Na_2CO_3	140	2.0% Na	150	1
T14D-46	Na_2CO_3	140	4.3% Na	200	3.8

TABLE XXIX (Cont'd)

Sample No.	Impregnant	Maximum Drying Temp. °C	Theoretical Metal Content	Sorption Temp. °C	SO_2 Sorbed Wt. %
T14D-47	Na_2CO_3	140	6.5% Na	200	3.5
T14D-48	Na_2CO_3	160	10.8% Na	200	8.6
T14D-23	Na_2CO_3	140	25% Na	100	6.0
				200	12.0
				300	15.0
T14D-24	Na_2CO_3	140	34.2% Na	200	6.0
				300	9.0
T14D-25	Na_2CO_3	140	40.0% Na	200	3
				300	4
T14D-26	K_2CO_3	140	38% K	200	3
				300	3
T14D-27	K_2CO_3	140	43% K	200	3
				300	2
T14D-28	K_2CO_3	140	49% K	200	3
				300	2
T14D-49	$NaHCO_3$	140	2.75% Na	200	3.1
T14D-50	$NaHCO_3$	140	4.1% Na	200	4.1
T14D-51	$NaHCO_3$	140	5.5% Na	200	4.1
T14D-52	$NaHCO_3$	140	8.2% Na	200	7.7
T14D-29	$NaHCO_3$	140	13.3% Na	200	6.5
				300	19
T14D-30	$NaHCO_3$	140	18.3% Na	200	13
				300	Caked
T14D-31	$NaHCO_3$	140	20% Na	200	9.5
				300	Caked
T5-3	NaOH	140	25% Na	200	2

is attributed to decomposition of calcium nitrate to calcium oxide on the silica gels, so that the sorptive capacity is due to the oxide rather than the nitrate.

A series of silica gels impregnated with sodium carbonate (T14D-46 - 48 and 23 - 25) showed increasing SO_2 sorption as the sodium carbonate content on the silica gel was increased (Tables XXX - XXXII). Maximum sorption occurred when 25 weight percent of sodium was impregnated on the silica gel. Higher sodium concentrations gave less sorption presumably due to blockage of the pores of the silica gel by the additional sodium carbonate. Low SO_2 sorption was also found in runs T14D-26, 27, and 28 in which three high concentrations of potassium carbonate were impregnated on silica gels. (Table XXIX)

Silica gels impregnated with sodium bicarbonate showed increased SO_2 sorptive capacity as the amount of sodium impregnated on the gel increased up to a maximum of about 13 weight percent sodium on the gel. The two samples impregnated with 18 and 20% Na as sodium bicarbonate caked in the evaluations at 300°C presumably due to decomposition of the sodium bicarbonate. (Table XXIX)

Run T5-3 is presented in Table XXIX to compare the sorptivity of a sample of silica impregnated with 25% Na with gels having the same sodium content. Because of silica's much lower surface area, it was a much poorer sorbent than silica gel.

3. Discussion

The data in Table XXIX show that the most active sorbents resulted when relatively strong bases were impregnated on the gel. This indicates that the sorption of SO_2 on these impregnated silica gels was not a physical adsorption but was instead a chemisorption in which SO_2 reacted with the basic cation. Because of cost considerations, impregnated sodium carbonate or bicarbonate silica gels would have to be regenerated, and the gel structure imposes severe limitations on a regeneration system. Wet systems can not be used because alkali-impregnated silica gels are not stable in water. When placed in water, the gels cracked and disintegrated. Thermal regeneration of sodium sulfites is not practical because the sulfite will disproportionate to the sulfide and sulfate. The latter is thermally stable far above the temperatures at which the silica gel structure is destroyed.

NOT REPRODUCIBLE

TABLE XXX

RUN 43 SORBENT T14D-46 (4.3% Na ON SILICA GEL)
ONE GRAM, TEMP. 200 DEG. C, FLOW 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
2.28	0.00	0.945E-02	0.010	0.277
2.61	1239.08	0.602E-02	0.013	0.342
2.95	2180.45	0.342E-02	0.014	0.384
3.61	2285.05	0.324E-02	0.017	0.440
3.95	2421.83	0.287E-02	0.018	0.467
4.28	2542.52	0.256E-02	0.019	0.490
4.61	2647.12	0.229E-02	0.019	0.511
4.95	2743.67	0.204E-02	0.020	0.530
5.28	2816.09	0.185E-02	0.021	0.546
5.95	2929.73	0.155E-02	0.022	0.576
6.61	3017.24	0.131E-02	0.023	0.600
6.95	3057.47	0.121E-02	0.023	0.611
7.61	3113.79	0.106E-02	0.024	0.630
7.95	3129.98	0.103E-02	0.024	0.640
8.61	3178.16	0.906E-03	0.025	0.656
9.61	3226.43	0.782E-03	0.026	0.678
10.28	3250.57	0.713E-03	0.026	0.691
11.61	3290.20	0.598E-03	0.027	0.713
12.61	3314.94	0.529E-03	0.028	0.728
13.61	3331.03	0.483E-03	0.028	0.741
14.61	3355.17	0.414E-03	0.029	0.752
15.61	3363.21	0.391E-03	0.029	0.762
17.61	3387.35	0.322E-03	0.030	0.781
18.61	3395.40	0.299E-03	0.030	0.789
19.95	3403.44	0.276E-03	0.031	0.799
20.95	3411.49	0.253E-03	0.031	0.806
40.61	3500.00	0.000E 00	0.038	1.000

NOT REPRODUCIBLE

TABLE XXXI

RUN 34 SORBENT T14D-47(7.5% Na ON SILICA GEL)
ONE GRAM, TEMP. 200 DEG. C, FLOW 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
3.26	0.00	0.970E-02	0.015	0.450
3.59	652.97	0.733E-02	0.018	0.530
3.93	957.47	0.706E-02	0.021	0.599
4.26	1182.75	0.645E-02	0.023	0.663
4.59	1617.24	0.523E-02	0.025	0.718
4.93	2059.77	0.400E-02	0.026	0.762
5.26	2381.60	0.309E-02	0.027	0.796
5.59	2614.94	0.243E-02	0.028	0.822
5.93	2783.90	0.196E-02	0.029	0.843
6.26	2912.64	0.161E-02	0.030	0.860
6.59	3001.14	0.136E-02	0.030	0.874
6.93	3073.56	0.116E-02	0.031	0.886
7.26	3137.93	0.989E-03	0.031	0.896
8.26	3234.48	0.738E-03	0.032	0.921
9.26	3306.89	0.551E-03	0.033	0.939
10.26	3355.17	0.414E-03	0.033	0.953
11.26	3379.30	0.345E-03	0.033	0.964
13.26	3427.58	0.207E-03	0.034	0.979
14.26	3435.63	0.184E-03	0.034	0.985
15.26	3451.72	0.138E-03	0.034	0.990
16.26	3459.76	0.115E-03	0.034	0.993
17.59	3475.86	0.690E-04	0.035	0.997
18.93	3483.90	0.460E-04	0.035	0.999
19.93	3499.99	0.293E-07	0.035	0.999
20.07	3500.00	0.000E 00	0.035	1.000

TABLE XXXII

NOT REPRODUCIBLE

RUN 55 SORBENT T14D-48(10.8% Na ON SILICA GEL)
ONE GRAM, TEMP. 200 DEG. C, FLOW 1000CC/MIN.

CALCULATED RESULTS - SO2 REMOVAL STUDY

TIME MIN.	SO2 EXIT CONCENTRATION (PPM SO2)	SORPTION RATE (GM SO2/MIN)	LOADING (GM SO2/GM SOLID)	FRACTION SORBED
0.00	0.00	0.000E 00	0.000	0.000
1.93	0.00	0.920E-02	0.008	0.102
2.26	8.25	0.941E-02	0.011	0.138
2.59	33.01	0.946E-02	0.015	0.174
2.93	1073.11	0.658E-02	0.017	0.205
3.26	1692.21	0.486E-02	0.019	0.227
3.59	1964.62	0.415E-02	0.021	0.244
3.93	2146.22	0.366E-02	0.022	0.259
4.26	2311.32	0.322E-02	0.023	0.273
4.59	2418.63	0.294E-02	0.024	0.284
4.93	2501.17	0.273E-02	0.025	0.296
5.59	2633.25	0.238E-02	0.027	0.315
5.93	2674.52	0.227E-02	0.028	0.324
6.26	2715.80	0.217E-02	0.028	0.333
6.93	2790.09	0.197E-02	0.030	0.349
7.59	2839.62	0.185E-02	0.031	0.363
8.60	2864.38	0.180E-02	0.033	0.385
9.26	2913.91	0.167E-02	0.034	0.398
9.60	2922.16	0.165E-02	0.035	0.404
10.60	2971.69	0.151E-02	0.036	0.423
11.60	3012.97	0.139E-02	0.038	0.440
12.60	3045.99	0.129E-02	0.039	0.455
13.60	3079.00	0.120E-02	0.040	0.470
15.60	3128.53	0.106E-02	0.042	0.496
16.59	3145.04	0.101E-02	0.043	0.508
17.93	3161.55	0.967E-03	0.045	0.523
18.59	3178.06	0.920E-03	0.045	0.530
19.93	3194.57	0.873E-03	0.047	0.544
20.59	3202.83	0.849E-03	0.047	0.551
21.93	3219.33	0.802E-03	0.048	0.563
22.93	3227.59	0.779E-03	0.049	0.572
24.26	3244.10	0.731E-03	0.050	0.584
25.59	3252.35	0.708E-03	0.051	0.595
26.26	3268.86	0.661E-03	0.053	0.616
29.59	3277.12	0.637E-03	0.054	0.626
33.93	3293.63	0.590E-03	0.056	0.657
35.93	3301.88	0.566E-03	0.058	0.670
36.26	3310.14	0.542E-03	0.058	0.672
69.14	3500.00	0.000E 00	0.086	1.000

One possible regeneration system that was considered was the reduction of sodium sulfite, which would form when SO_2 would react with sodium hydroxide or bicarbonate, by a mixture of hydrogen and carbon monoxide. Based on the yields of water and CO_2 obtained when silica gel impregnated with 10% Na_2SO_3 was reduced at 550°C with an equimolar mixture of hydrogen and CO, over 93% of the sodium sulfite on the gel was reduced to sodium sulfide in one hour. Analysis of the resulting redried gel showed that 97% of the sulfite was reduced. The sodium sulfide could then be converted to sodium carbonate.

Unfortunately, the reduction with hydrogen and CO had to be conducted at 550°C or 1000°F which is near the temperature at which gel structure begins to break down due to dehydration. This ruled out any possible use of silica gels in such a regenerative sodium carbonate system.

The original aim of this study was to find a promoter which would oxidize the SO_2 to SO_3 on the silica gel so that the resultant sulfuric acid could be stored in the silica gel. This was not achieved.

Sodium carbonate sells for $32/ton, silica gel for approximately $600/ton. It therefore made better economic sense to consider systems using sodium bicarbonate and sodium carbonate themselves rather than using these materials on an expensive support. Thus, while these studies did not yield the intended results, they did provide the impetus for developing the Na_2CO_3 system evaluated below.

I. HYDROXIDES

Several hydroxides have been mentioned for their ability to remove oxides of sulfur from gas streams. Perry[47] reported that a ferric hydroxide gel adsorbed an amount of SO_2 from an SO_2-air mixture equal to 10.9% of its weight. Japanese patent 11648/68[48] cites ferric hydroxide as being a satisfactory adsorbent for SO_2 while Belgium patent 692466[49] states that iron hydroxide is only one of a number of hydroxides which are suitable for adsorbing SO_2. This patent claims that hydroxides of aluminum, manganese, alkaline metals and alkali earth metals are also adsorbents for SO_2. The use of manganese hydroxide as an adsorbent for SO_2 was also described in Japanese patent 14712/67[50].

In the recommended program for Phase II work, it was suggested that ferric hydroxide sorbents be investigated because of these various reports of its reactivity with SO_2 in stack gases. However, at the Cincinnati meeting of the Contractors it was decided that only minimum work should be done on iron hydroxide because this represented a border area between iron hydroxides and iron oxides which is outside the scope of this contract. Calcium and magnesium hydroxides were eliminated from consideration because of the extensive work being done by other contractors on dolomites.

Unlike iron oxides, iron hydroxides are not available commercially. Iron hydroxide was prepared by alkalizing ferric chloride solutions with sodium hydroxide and ammonia hydroxide. The resulting participates were filtered and dried both in a vacuum at 60°C and in an oven at 140°C. The yields of hydroxides were approximately stoichiometric for the hydroxides dried in a vacuum and about 78% for those dried at 140°C in air. Presumably some dehydration occurred during the latter preparations even though the handbook states that ferric hydroxide does not lose water below 500°C.

The results of the sorption of SO_2 on iron hydroxide are shown in Table XXXIII.

TABLE XXXIII

Sorption of SO_2 on Iron Hydroxides

Sample No.	Preparation Method	Sorption Temp. °C	SO_2 Sorbed Wt. %
T4-1	$Fe(OH)_3$ precipitated from $Fe(NO_3)_3$	23	4.9
	with NaOH, dried at 60°C in vacuum	100-125	4.4
T4-2	Same as above, but $(Fe(OH)_3$	23	3.5
	precipitated with NH_4OH	100-125	5.8
T4-4	Same as T4-1, but dried at	23	0.7
	140°C in air	100-125	0.5
T4-3	Same as T4-2, but dried at	23	2.0
	140°C in air	100-125	0.7

Hydroxides prepared in vacuum sorbed about 5 weight percent of SO_2, those heated to the higher temperatures sorbed less than 1 weight percent SO_2 at 100 to 125°C. The difference in sorptive capacities probably is related to the presence of the gel structure in the samples dried at the lower temperatures. Two samples of commercial iron oxide, evaluated to compare their activities with those obtained with the hydroxide samples, sorbed less than 1 weight percent of SO_2.

The SO_2 sorption capacity of iron hydroxide depends on the presence of the hydroxide gel structure as opposed to the oxide form. Ferric hydroxide powders easily. To be used in a practical system, ferric hydroxide would have to be made granular or pelleted. No regeneration system that does not go through the oxide stage can be visualized and this probably would place these materials outside the scope of this contract.

Because of the narrow temperature range in which these materials must be prepared without forming the oxides and the inability to develop a sound, economical regeneration scheme, the use of hydroxides as SO_2 sorbents does not appear to be promising.

SECTION III - DESORPTION OF SORBED SO_2 FROM CARBON

A. INTRODUCTION

The Reinluft, Sulfacid (Lurgi) and Hitachi processes all use activated carbon as a sorbent for SO_2 from flue gases[44]. The effectiveness of active carbon as a general purpose adsorbent correlates well with surface area, but there is no correlation between surface area and the effectiveness of various carbons as SO_2 sorbents from stack gases.

Carbon-based flue gas treating processes are attractive because the sorptive capacity of carbon for SO_2 from stack gas is several fold greater than its capacity to sorb pure SO_2 at the same total pressure. The high capacity of carbon for SO_2 from stack gas is the result of a complex series of chemical reactions which consume water and oxygen as well as sulfur dioxide (Juntgen & Dratwa).[51,52,53,54,55]

Certain sites on the carbon surface hold localized unpaired electrons. These sites, which can be detected by electron spin resonance spectroscopy, are active catalysts for the combination of sorbed sulfur dioxide with sorbed oxygen. This reaction produces sulfur trioxide as a sorbed species. This, in turn, reacts with sorbed (or gaseous) water to form sulfuric acid.

Even at usual stack gas temperatures, the sulfuric acid is well below its dew point. Accordingly, it forms a condensed phase which is held within the pore structure of the carbon by capillary forces. The acid establishes an equilibrium with the water vapor in the stack gas. Typically the acid sorbed within the pore structure contains about 30% water by weight (1.8 mols H_2O per mol H_2SO_4).

Carbon owes its uniqueness to its ability to function as an oxidation catalyst and as an inert matrix to hold the sulfuric acid that is formed on oxidation and reaction with water. This sorption process cannot be viewed in terms of the conventional concepts of adsorption as usually applied to sorption of gases on carbon, and the concept of an equilibrium sorption isotherm for SO_2 from stack gas on carbon is meaningless. Instead, the process must be approached in terms of the concepts of chemical kinetics in which saturation of the carbon corresponds to the filling-up of the carbon pores with sorbed acid. The active surface of the carbon occludes acid and so decreases the rate of sorption.

The kinetics of the overall reaction (sorption) actually change in the temperature range of interest. At low temperatures, the surface is essentially saturated with SO_2 and oxygen, and the rate is limited by the kinetics of the SO_2 oxidation step. As the temperature is increased, the SO_2 oxidation rate increases and thus the overall reaction rate increases. As the temperature is increased further, the overall rate eventually begins to fall because the sorption of SO_2 on the carbon surface decreases with increasing temperature. Eventually, a point is reached at which the sorbed SO_2 concentration on the surface of the carbon is so low that it limits the rate of the overall reaction. The maximum rate occurs at temperatures between 100 and 125°C which is ideal for treating stack gases.

The regeneration of carbon saturated with H_2SO_4 is also a complex process. To date, two methods have been used. The simplest of these is washing, which is used by the Sulfacid and Hitachi processes. Water is trickled through a bed of saturated carbon and leaches the acid from the carbon particles. Unfortunately, the maximum acid concentration achievable in the leach liquor is rather low. The problem of low acid concentration arises since the liquor no longer wets carbon particles at an acid concentration of between 10 and 20 percent. Because dilute acid has limited economic value, regeneration of carbon by washing is unattractive.

The second regeneration method is thermal regeneration. The sulfuric acid saturated carbon is heated to a temperature at which the carbon reduces the sulfuric acid forming sulfur dioxide, carbon dioxide, and water. Chemically, the process appears fairly complex (Juntgen)[52]. The regeneration process does not proceed at a reasonable rate below about 650°F. In the course of heating the saturated carbon to this temperature, the sorbed acid is concentrated to essentially pure H_2SO_4. Thus, it appears that the first step in regeneration is:

$$H_2SO_4 \rightarrow SO_3 + H_2O$$

The second step appears to be the reaction of gaseous sulfur trioxide with the carbon surface to form sulfur dioxide and the carbon "surface oxide". This oxide appears to be a covalently bonded oxygen atom attached to a carbon atom on the surface which is still bonded to the carbon matrix by a pair of covalent bonds.

The surface oxide site apparently can react further with a second sulfur trioxide to form carbon dioxide and sulfur dioxide.

$$SO_3 + C \rightarrow (>C{=}O) + SO_2$$

$$(>C{=}O) + SO_3 \rightarrow CO_2 + SO_2$$

Several observations support this mechanism. Under certain conditions, it is reported that the majority of the sulfur values can be recovered as sulfur trioxide. This suggests that the trioxide is the initial desorbed product. The other observation is that virtually no free carbon monoxide is produced on regeneration unless the carbon is heated to temperatures above 450°C.

The principal drawback to the desorption of sulfuric acid or SO_2 from carbon by thermal methods is that the carbon on repeated recycling becomes pyrophoric during use. This pyrophoricity is usually associated with the loss of carbon by reaction with sulfuric acid which condensed on the carbon surface, as described above. The increased pyrophoricity of the carbon results in combustion within and destruction of the sorbent bed. Based on the stoichiometric reactions shown in equations 3 through 6 in Table XXXIV 6 to 12 pounds of carbon are consumed for every 32 pounds of sulfur desorbed from the carbon.

There are two possible methods to overcome the pyrophoricity of the sorbent bed. The Chemiebau Company, as described in the literature survey[19,20], controls temperatures within the carbon bed by mechanical means. However, this requires a more complicated reactor and regeneration system and, with its two conveying systems, requires much higher capital investment and increased power costs. Since the capital investment of the Reinluft process was high originally, the additional fabrication adds additional costs to a sulfur recovery process that already suffered from high capital requirement.[56]

Another potential approach to the regeneration of carbon is the use of reducing gases which would reduce the SO_3 and/or sulfuric acid to SO_2. A series of the major reactions for the desorption of sulfuric acid from carbon are shown in Table XXXIV.

Simple adsorption and desorption of SO_2 undoubtedly occur to a very significant extent but, as far as can be determined, have no affect on the carbon surface. SO_2 that is adsorbed and oxidized to either sulfuric acid or SO_3 might be removed as shown in reactions 1 and 2. However, the equilibrium constant for the decomposition of SO_3 to SO_2 and oxygen is unfavorable at 427°C, the temperature at which oxides of sulfur are desorbed from carbon in the Reinluft Process.

Reactions 3 and 4 both show reaction between sulfuric acid and carbon to form SO_2 with the formation of CO and CO_2. Reaction 3 is believed to be the predominant reaction between sulfuric acid in reactions 3 and 4. Reactions 3 through 6 all consume carbon and therefore contribute to its consumption and ultimate pyrophoricity.

Reactions 7 through 10 show the thermodynamic feasibility of reducing sulfuric acid or sulfur trioxide with either hydrogen or carbon monoxide. The use of these reducing gases produces SO_2 without causing reaction of either sulfuric acid or sulfur trioxide with carbon. If a regeneration process were based on the use of H_2 or CO reducing gases, or a reducing gas mixture such as producer gas, it might improve the operability of a carbon-based adsorption process. The equilibria constants in Table XXXIV are highest for reactions 7 through 10, which suggests an excellent possibility for any or all of these reactions to occur. To explore the nature of the kinetics of reactions involving reducing gases, a study of the desorption of adsorbed SO_2 from carbon with hydrogen was initiated.

B. EXPERIMENTAL

1. Thermogravimetric Analyzer (TGA) Studies on The Desorption of SO_2 From Carbon

Weight losses during desorption of SO_2 from carbon were investigated on a TGA instrument. The TGA weighs samples with an extremely accurate Cohn R6 electrobalance. With this

TABLE XXXIV

Equilibrium Constants[1] @ 427°C (700°K) of The Major Reactions for The Desorption of H_2SO_4 From Carbon

Reaction			K_{eq} @ 700°K	
H_2SO_4	=	$SO_2 + H_2O$	0.7	(1)
SO_3	=	$SO_2 + 1/2\ O_2$	4.8×10^{-3}	(2)
$H_2SO_4 + 1/2\ C$	=	$1/2\ CO_2 + SO_2 + H_2O$	3.5×10^{12}	(3)
$H_2SO_4 + C$	=	$CO + SO_2 + H_2O$	6×10^{9}	(4)
$SO_3 + 1/2\ C$	=	$1/2\ CO_2 + SO$	4.5×10^{12}	(5)
$SO_3 + C$	=	$CO + SO_2$	7.8×10^{9}	(6)
$H_2SO_4 + CO$	=	$H_2O + SO_2 + CO_2$	2×10^{15}	(7)
$H_2SO_4 + H_2$	=	$2H_2O + SO_2$	1×10^{13}	(8)
$SO_3 + CO$	=	$SO_2 + CO_2$	2.5×10^{15}	(9)
$SO_3 + H_2$	=	$SO_2 + H_2O$	1.4×10^{13}	(10)

[1] Calculated from Tracor, Inc. data[57]

balance, the rate and amount of weight change were noted during both sorption and desorption of SO_2, as well as changes in the carbon weights before and after the desorption.

The carbon sample was held in a Quartz basket capable of holding up to 14 mg. The Reinluft process employs an active coke as an SO_2 sorbent; but since no coke tested in our laboratory had a sorptive capacity approaching that of the Reinluft material, our studies were made with activated carbons rather than coke.

a. Low Temperature TGA Sorption - Desorption Studies

Pittsburgh carbon type BPL, 12 x 30 mesh material was chosen for these studies. This moderately dense carbon sorbed 8-10 weight percent SO_2 at room temperature.

The carbon was dried by being heated to 150°C, cooled to room temperature, and then allowed to sorb SO_2 from a mixture of 1% SO_2 in helium until the carbon ceased to gain weight. The carbon was then heated to a temperature at which further desorption of SO_2 ceased. Data obtained on the TGA apparatus is shown in Table XXXV. Series A showed that the original carbon contained from 7 to 8 weight percent moisture. The dried carbon sorbed 7.5 weight percent SO_2; and the weight loss observed on heating the carbon on which SO_2 had been adsorbed to 250°C was less than the weight of SO_2 which was apparently adsorbed. All weight loss occurred below 150°C.

Series B in Table XXXV shows the weight history of SO_2 sorbed and desorbed on undried carbon. In the first part of each experiment, the weight gain resulting from SO_2 sorption varied from 0.5 to 1.8 weight percent of carbon charged. This low gain in weight when SO_2 was sorbed on undried carbon reflects the net effect of loss of moisture and adsorption of SO_2. After the sample had been heated to 150°C to desorb the adsorbed SO_2, the gain in weight due to SO_2 adsorption on subsequent cycles varied from 7 6 to 7.9%, which is essentially the same as that which was obtained in series A when dry carbon was used. Successive SO_2 sorptions and desorptions showed essentially the same data as was obtained in series A with the amount of SO_2 desorbed still being less than that which was sorbed.

TABLE XXXV

Summary of TGA Studies on The Sorption and Desorption of SO_2 on Pittsburgh BPL Carbon

Series A Sorption and Desorption of SO_2 on Dry Carbon in Helium

Experiment Number	I	II
Loss on Pre-conditioning Heating to 150°C Weight %	6.8	7.7
SO_2 Adsorbed on Dried Carbon at 25°C from 1% SO_2 in Helium, Weight %	7.5	7.5
SO_2 Evolved on Heating to 150°C, Weight %	7.2	7.2
SO_2 Evolved on Heating from 150 to 250°C	None	None

Series B Sorption and Desorption of SO_2 on Undried Carbon in Helium Sorption Gas Stream - 1% SO_2 in Helium

Experiment Number	I	II
	Carbon Weight Change, Wt. %	
Sorption at 30°C	+0.5	+1.8
Desorption - Heated to 150°C	-7.0	-7.4
Cooled to 30°C, SO_2 Sorption	+7.9	+7.6
Desorption - Reheated to 150°C	-7.5	-7.5
Cooled to 30°C, SO_2 Sorption	+7.8	-
Desorption - Reheated to 150°C	-7.6	-

Series C Adsorption of SO_2 From Moist Helium

	A	B
Sorption of Moisture, Weight %	32.9	27.8
Sorption of SO_2, Weight %	1.4	
Loss in Heating to 150°C, Weight %	33.3	25.5
Loss in Heating from 150 to 400°C, Weight %	6.2	9.8

To check the effects of moisture on SO_2 sorption on carbon, helium that had been bubbled through water was passed into the reactor system until the carbon ceased to adsorb moisture and a 1% SO_2 in helium stream was then bled into the moist helium stream. The data in series C showed a considerable weight gain due to the sorption of both water and SO_2. Unlike the earlier runs, a substantial amount of material was evolved when the carbon was heated from 150 to 400°C. The much higher weight loss found when the carbon was heated from 150 to 400°C (when all water presumably had been removed) suggests that SO_2 and water plus oxides in the carbon formed H_2SO_4 which was only removed at the higher temperatures.

These results indicated that a reversible physical adsorption of SO_2 was the principal reaction when SO_2 was sorbed on dry carbon. The small loss of SO_2 was attributed to the formation of chemisorbed species on the surface of the carbon with active oxygen sites and/or residual moisture. In subsequent work, it was found that recovery of all SO_2 was not obtained even after 10 successive adsorption - desorption cycles in the absence of moisture and air.

In the presence of moisture, the SO_2 reacted with the moisture and active oxygen sites to form H_2SO_4 which was desorbed only at temperatures well above 150°C with the most rapid weight loss occurring near 300°C. Part of the weight loss that occurred at these elevated temperatures may have been due to reaction of H_2SO_4 with carbon but this could not be determined as these studies were carried out.

b. High Temperature TGA Studies on Desorption of SO_2 From Carbon

The low temperature TGA studies made by sorbing SO_2 at room temperature were inconclusive because of competing reactions. Thus, the presence of sorbed moisture on carbon masked the amount of SO_2 that was sorbed because some moisture was desorbed as the SO_2 was being sorbed. To eliminate water effects, the desorption was studied in the 170°C to 350°C temperature range. This approach, described in a memo from L. R. Beck to L. D. Friedman in Appendix II, gave a clearer picture of the reactions that occur during the desorption of SO_2 from carbon.

The TGA techniques described by Beck involved heating carbon at 350°C until no weight loss was obtained for a period of at least ten minutes, cooling to room temperature and then passing moist helium through the carbon bed. This continued for one hour, during which time the carbon weight increased about 15 weight percent. One percent of SO_2 in helium was then passed through the carbon for a half-hour while the moist helium flow was continued. As in the earlier work, the quantity of SO_2 adsorbed was not known because some water was lost during the SO_2 sorption period. However, experience with dry helium showed that about 6 weight percent of SO_2 was sorbed by the carbon under the same operating conditions.

The carbon was then heated at 6°C per minute and the weight of material evolved between 170°C and 350°C was determined. The 170°C point was chosen because experiments showed that essentially all water was desorbed from carbon at this temperature when SO_2 was not present. The material retained on the carbon at temperatures above 170°C was probably SO_3, sulfuric acid or chemisorbed SO_2.

The TGA experimental results are summarized in Table XXXVI. In a sorption-desorption cycle with dry inert gases, a weight loss of about 0.1% of the carbon was found. This is close to the minimum weight loss that can be detected by the TGA and may be due to the buoyancy effect of the gas. When moisture is added to inert gases in the sorption cycle, the weight loss per cycle was 0.4 weight percent, which was only slightly less than that obtained when SO_2 was added from dry gases. The weight loss increased progressively as SO_2 was added with air, moisture, and moisture plus air. Moisture and air both were synergistic to carbon weight loss with SO_2. Thus, the weight loss after sorption in the presence of moisture and SO_2 is much greater than the sum of losses obtained with moisture and SO_2 alone, and that obtained with moisture, SO_2 and air is greater than that obtained with moisture, and with SO_2 and air. These results are similar to those reported in Dratwa's thesis.[51] However, the losses from reaction of carbon with moisture alone was much higher than that obtained with inert gas, and confirms the finding that wasting of carbon is not due only to reaction with SO_2 and other oxides of sulfur.

TABLE XXXVI

Weight Loss Between 170°C and 350°C From Sorption-Desorption Cycles with Nuchar Carbon

Sorbent Mixture	Desorbing Mixture	% Loss Between Temp. Range of 170-350°C
Dry He	Dry He and N_2	0.1
Moist He	Moist He and N_2	0.4
Dry He-N_2-SO_2	Dry He-N_2	0.5
Dry He-SO_2-Air	Dry He-N_2	0.7-0.8
Moist He-SO_2	Moist He-N_2	2.1
Moist He-SO_2	Moist He-H_2	1.9
Moist He-SO_2-Air	Moist He-N_2	3.0
Moist He-SO_2-Air	Moist He-H_2	3.2

Table XXXVI also shows that the carbon weight losses obtained in desorptions carried out in a hydrogen atmosphere are not smaller than those obtained in a nitrogen atmosphere. Unlike other studies described below, the nitrogen appeared to remove the sulfur faster than the hydrogen. The reason for this difference is not known, but may be related to the different carbons used in the two studies.

Perhaps the most important finding in these studies was that carbon losses during desorption of SO_2 in a reducing gas were not lower than similar losses in an inert medium. This was confirmed further, as described below.

2. Macro Carbon Sorption - Desorption Studies

a. Weight Losses on Repeated Cycles

To study the adsorption and desorption of SO_2 from carbon on a larger scale than was possible in the TGA apparatus, about 5 grams of carbon was placed in a stainless steel basket which was suspended inside a 1" stainless steel pipe heated by a Hoskins-type furnace.

One approach in these studies was to conduct a series of adsorption and desorptions, and to note changes in weight in the carbon resulting from several adsorption-desorption cycles. It was hoped that information concerning the relative rate and efficiency of desorption of SO_2 in nitrogen and hydrogen media could be determined, and that differences in the weight of the carbon before and after the experiments would give some indication of whether reducing gas gave a lower weight loss than inert atmospheres.

The results of these studies were inconclusive. Sorption of SO_2 from a synthetic flue gas sample was conducted at 150°C, desorption at both 350 and 450°C. There was neither a consistent pattern of weight losses with time nor an effect arising from the use of a reducing gas. In addition, weight losses resulting from reaction of carbon with gases other than SO_2 could not be determined.

3. MS Analyses of Product Gases

a. Introduction

Another approach to this problem was to analyze for CO_2 and/or CO that was evolved when H_2SO_4 reacted with carbon during a thermal desorption cycle.

$$C + H_2SO_4 \rightarrow CO + SO_2 + H_2O \qquad I$$

$$C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O \qquad II$$

In reaction I, one mol of CO is formed per mol of sulfuric acid. In reaction II, one-half mol of CO_2 is formed per mol of sulfuric acid.

Calculations showed that if only one-tenth gram of a 10 gram carbon sample (1%) reacted with sulfuric acid, the amount of CO or CO_2 that would be formed would be sufficient to be detected by mass spectrographic analysis. Thus, some indication of the rate of consumption of carbon by sulfuric acid could be obtained.

If reducing gases such as hydrogen or CO reduced the amount of reaction that occurred between sulfuric acid and carbon, according to Equations I and II above, then significant differences in the quantities of CO or CO_2 evolved should have been detected. To study these, mass spectrographic analyses were made on gas samples evolved during the desorption cycle in the presence of hydrogen, a reducing gas, and helium, an inert gas.

This approach measured only total CO or CO_2 evolved and thus did not differentiate between CO or CO_2 evolved from reaction of H_2SO_4 with carbon and that resulting when carbon that had been exposed to oxygen at one temperature was heated to a higher temperature. In our experiments, SO_2 sorption was conducted at about 125°C in the presence of 3-4 mol percent of oxygen and 4-6 mol percent of moisture, and desorption was carried out at 350°C. Because of the 350°C desorption temperature used in these studies, it was possible that CO or CO_2 would be evolved during the sorption-desorption thermal cycles used due to reaction of the carbon with the oxygen and moisture in the synthetic flue gas.

b. Experimental Procedure

A 10 gram sample of Pittsburgh BPL carbon was placed in an electrically-heated stainless steel pipe and moist, synthetic flue gas was passed through the carbon at 125°C until SO_2 sorption ceased. The bed was then heated at the constant rate of about 3°C per minute while purge gas was bled through the carbon bed. Composite gas samples were collected while the sample was being heated to 200°C, from 200 to 250°C, from 250 to 300°C, from 300 to 350°C, and a final sample was taken while the carbon was heated for 15 minutes at 350°C. To keep dilution of the product gases to a minimum, a purge gas rate of only 40 cc per minute was used in the desorption experiments. Hydrogen was the reducing gas used in this experiment and helium was the inert gas. Helium was used because its peak on the mass spectrograph would not interfere with any of the other peaks that might be found. Nitrogen would have the same mass as carbon monoxide and would have masked the latter's presence.

c. Experimental Results

The bar graphs in Figure 8 show the relative rates at which SO_2 was desorbed as the temperature was increased. In runs A and B, the gas sample evolved while the bed was being heated to 200°C contained 2% O_2, 7% CO_2, and much SO_2. These obviously came from inadequate flushing of the synthetic flue gas from the system before starting the desorption. When the experiments were repeated (runs C & D) and the carbon was flushed with a flowing stream of helium at room temperature before the heating for the desorption operation was started, the gases collected below 200°C had no O_2 or CO_2 and only traces of SO_2.

The data in Figure 8 show that SO_2 was consistently removed at a lower temperature with hydrogen than with helium. The reason for this phenomenon is not known but, as mentioned above, it was observed in other studies as well.

The analyses for the paired runs made with hydrogen and helium are shown in Table XXXVII. Both runs showed a constant lowering of the SO_2 to CO_2 ratio as the temperature was increased. The amount of CO_2 evolved was far greater than that attributable to reaction of H_2SO_4 with

FIGURE 8

Desorption of SO_2 From Carbon in Hydrogen and Helium Atmospheres

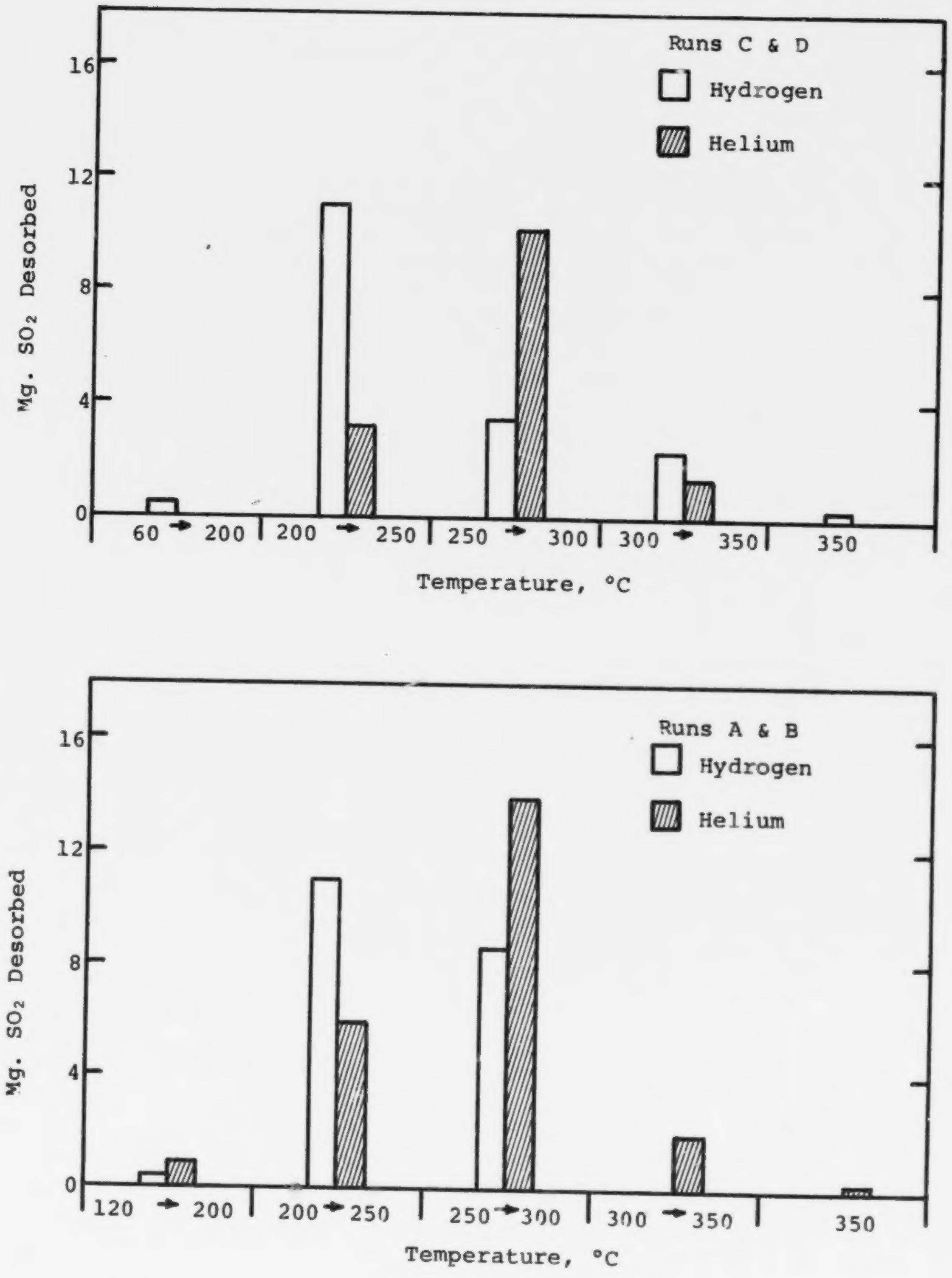


TABLE XXXVII

Mass Spectrographic Analyses of Desorption Gas Composites

RUN	C				D			
DESORBING GAS	HELIUM				HYDROGEN			
PRODUCT GASES, Mol %	O_2	SO_2	CO_2	$SO_2:CO_2$ Ratio	O_2	SO_2	CO_2	$SO_2:CO_2$ Ratio
TEMPERATURE RANGE, °C								
60 - 200	0.52	-	0.90	-	1.5	0.2	0.09	2.2:1
200 - 250	-	0.42	0.50	0.84:1	0.3	0.68	0.39	1.7:1
250 - 300	-	0.37	0.54	0.69:1	0.3	0.12	0.12	1:1
300 - 350	-	0.04	0.38	0.1:1	-	0.12	0.26	0.46:1
350	0.05	0.05	0.23	-	-	0.01	0.09	0.11:1

carbon and must have resulted from decomposition of carbon-oxygen complexes formed during the adsorption cycles. Formation of CO_2 by such mechanisms is well documented in carbon literature. No carbon monoxide was found in any of the MS analyses.

The sulfur balances in these runs were not closed. Some SO_2 was lost in sampling and some in the mass spectrometer where it clings to the wall of the instrument. In addition, evolved water could not be determined in the experimental procedure. To obtain more precise analytical data, the desorption of SO_2 was followed by VPC techniques, as described below.

4. VPC Analyses of Product Gases

Gas samples submitted for the mass spectrographic analyses discussion above were collected in gas bottles. This resulted in loss of SO_2 and moisture.

Vapor phase chromatography offered a convenient method for eliminating these losses. The VPC instruments were connected to the gas line leading from the SO_2 desorption reactor. No sample storage in gas bottles was required, and by using appropriate switching valves and different columns, CO, CO_2 and SO_2 could be determined every six minutes.

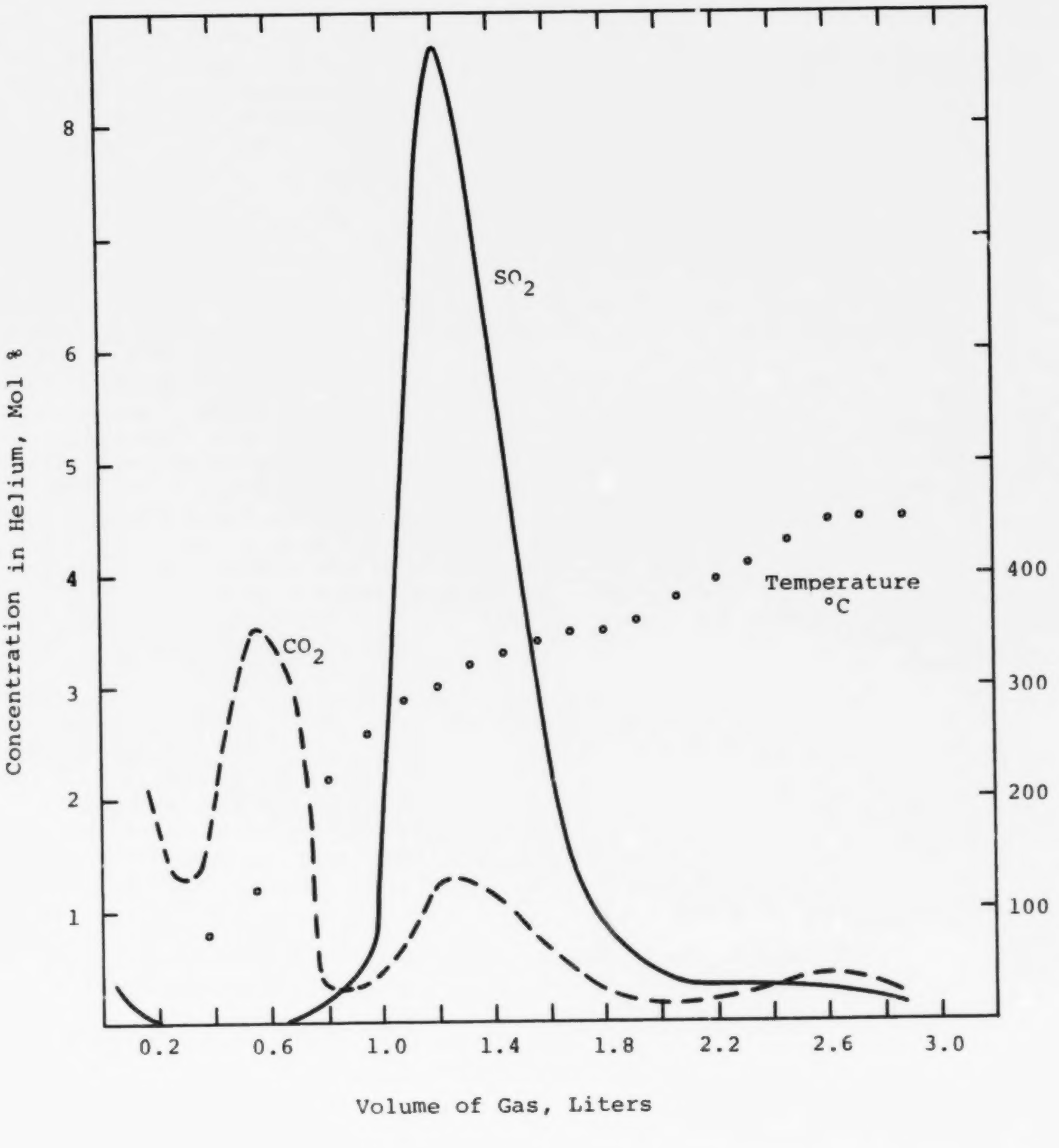
In the actual set-up used, effluent gases from the carbon columns were passed through magnesium perchlorate to remove water and then through three VPC units in series to determine SO_2, CO_2 and CO. The magnesium perchlorate tubes were weighed after each 50°C temperature rise. The VPC analyses were made for all three gases every six minutes. The sorption and desorption cycles were the same as those used in the MS studies reported above.

SO_2 from synthetic flue gas was sorbed on 10 grams of Pittsburgh BPL carbon at 125°C. The carbon was cooled to 50°C and the sweep gas used in the various experiments was passed through the carbon bed while the carbon was heated at 3-5°C per minute.

Figure 9 shows the rates of evolution of gases as the carbon bed was heated in a flowing helium atmosphere. At temperatures below 80°C, unsorbed water, CO_2 and SO_2 were swept out of the system. Between 80 and 200°C adsorbed CO_2 was evolved, with maximum evolution occurring about 145°C.

Figure 9

Desorption of SO_2 From Carbon in Helium



This CO_2 could include desorbed CO_2 plus any that might have formed by the reaction of carbon with oxygen complexes on the surface. No water was found at temperatures below 200°C, and no SO_2 was present until a temperature of 175°C was reached. About 90% of the SO_2 that was evolved was collected while the carbon was being heated from 250 to 350°C. CO_2 evolution reached a peak at about 325°C, but the quantity of CO_2 evolved was only about one-third that which should have been obtained if all the SO_2 had been formed by reaction of sulfuric acid with carbon, according to equation 2 on page 91. Above 350°C, SO_2 evolution became negligible but CO_2 evolution rose and exceeded SO_2 evolution at 450°C. This CO_2 probably originated from rupture of C-O surface complexes. Traces of CO were found beginning at 400°C and these continued until the 450°C temperature was reached.

The corresponding curves for the desorption of SO_2 and CO_2 in a hydrogen atmosphere are shown in Figure 10. Again adsorbed CO_2 was removed most rapidly at a temperature of between 120°C and 150°C. The first traces of SO_2 occurred at about 120°C which was about 50° lower than in the helium run. The most noticeable difference in these two runs is the formation of less CO_2 in hydrogen than in helium. In hydrogen too, as in helium, water evolution did not start until a temperature of 200°C was reached.

The production of gases in the 200-350°C range where maximum SO_2 evolution occurred, is shown in Table XXXVIII. Assuming that all CO_2 collected in this temperature range came from reaction of H_2SO_4 with carbon, it can be seen that in the presence of helium there is a deficiency of about 15% of the water needed to account for the CO_2-forming reaction. This deficiency is probably within experimental error. In the hydrogen atmosphere, the quantity of water collected is almost twice that needed for CO_2 formation. This excess water might have formed either by reduction of surface oxides with H_2 or by reaction of H_2 with H_2SO_4 or SO_3.

In both runs the amount of SO_2 in excess of that accounted for by a CO_2-forming reaction was quite substantial. This should be physically adsorbed SO_2, but could include some SO_2 formed by reduction of H_2SO_4 or SO_3 with H_2.

Figure 10

Desorption of SO_2 From Carbon in Hydrogen

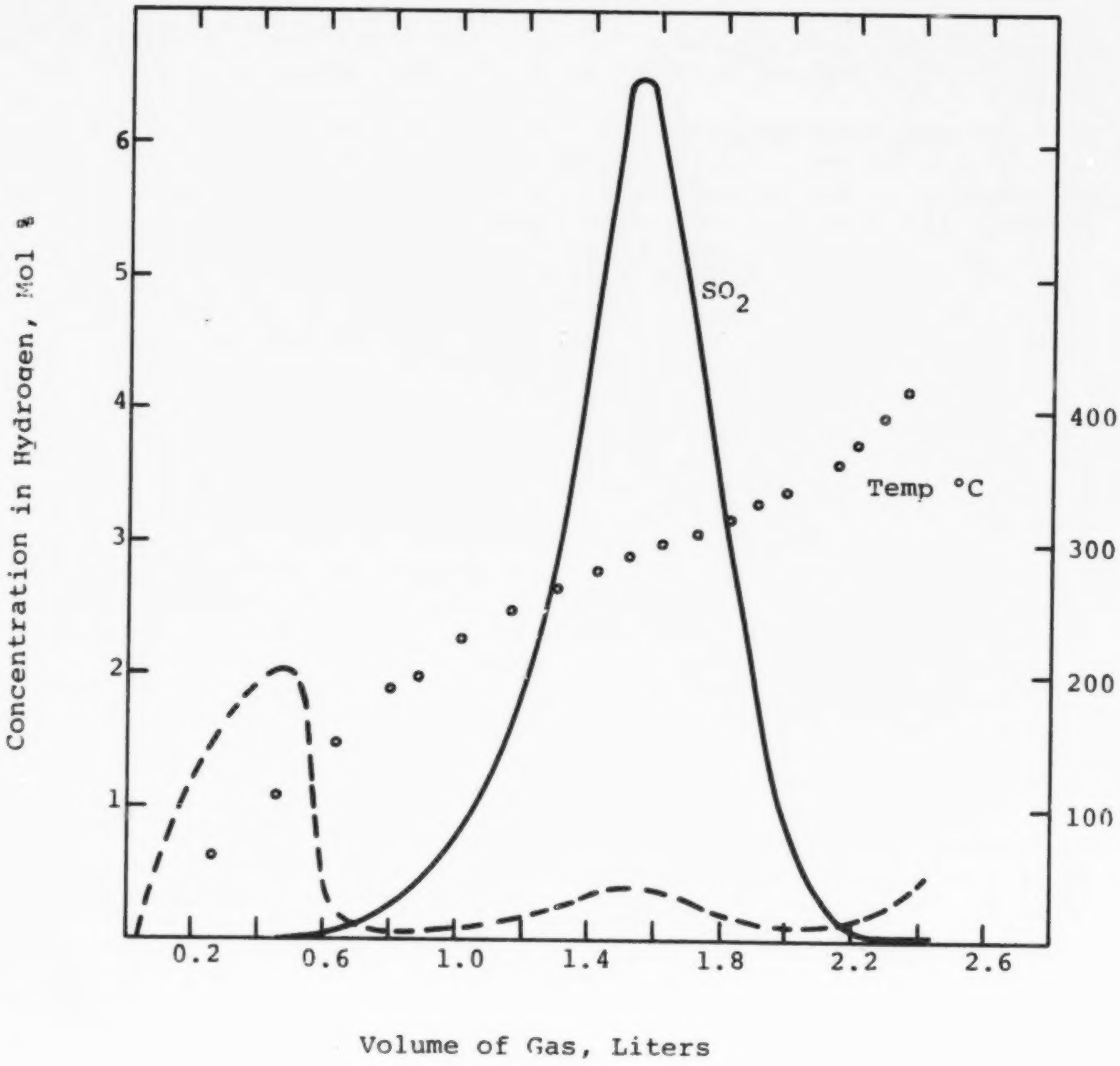


TABLE XXXVIII

Evolution of Gases During Desorption of SO_2 From Pittsburgh BPL Carbon

Helium

	CO_2	H_2O	SO_2
Gases Evolved between 200 and 350°C, millimols	0.54	0.93	1.95
Calculated Gas Evolution according to C - H_2SO_4 reaction,[1] millimols	0.54	1.08	1.08
DIFFERENCE	-	-0.15	+0.87

Hydrogen

	CO_2	H_2O	SO_2
Gases Evolved between 200 and 325°C, millimols	0.12	0.45	1.73
Calculated gas evolution according to C - H_2SO_4 reaction,[1] millimols	0.12	0.24	0.24
DIFFERENCE	-	+0.21	+1.49

[1] $C + 2H_2SO_4 \rightarrow CO_2 + 2H_2O + 2SO_2$

C. DISCUSSION OF CARBON REGENERATION STUDIES

Both the TGA and the larger scale studies reveal the complexity of the SO_2-carbon reaction. This definitely is not a simple physical sorption in which SO_2 is sorbed at a low temperature and desorbed at a higher temperature. The sorption of SO_2 depends on a chemisorption reaction which varies with the presence of other materials. Thus, dry SO_2 sorbed on clean, outgassed carbon may be largely desorbed when the carbon is heated. (See Table XXXVI above.) However, as the concentration of water and/or oxygen in the SO_2-containing gas stream is increased, less SO_2 is physically sorbed. Instead, the SO_2 reacts with oxygen and/or moisture to form H_2SO_4 (or SO_3) and these do not desorb from the carbon surface as readily as dry SO_2. For complete removal of H_2SO_4, a reducing agent is required, and this is usually the sorbent carbon which reacts at the desorption temperatures.

Desorption of SO_x from carbon with hydrogen was not more effective than with inert gases such as nitrogen or helium. Since the SO_x is present as sulfuric acid inside the pores of the carbon, contact between the desorbing medium (gas) and the sulfuric acid is worse than the contact between the sulfuric acid and the carbon inside the pores. Therefore, the kinetics of the reaction probably favor reaction between H_2SO_4 and carbon and the character or nature of the gas medium is relatively unimportant.

There was one major difference in the results obtained with the TGA apparatus and those obtained in the larger scale VPC and MS studies. On the TGA, hydrogen did not desorb SO_2 faster than did nitrogen or helium. However, in all three studies made in the larger reactor, hydrogen desorbed SO_2 at a lower temperature than either helium or nitrogen. The reasons for these differences are not known. One explanation might be a matter of reactor geometry. In the macro reactor, the gases were passed through the bed of carbon whereas in the TGA apparatus, the desorbing gases passed up through a tube in which the carbon particles were suspended in a quartz basket. Thus, the contact between the sweep gases and the carbon was different in the two reactors. Another difference was the fact that different carbons were used in the two reactors. In the macro studies, a Pittsburgh carbon having the maximum SO_2 sorptive capacity was used whereas in the TGA studies a dense Nuchar carbon was used in order to obtain a greater weight of carbon in a given reactor.

The effect of different carbons on sorption and desorption characteristics is quite marked. Dratwa and Juntgen[65] compared the calculated and theoretical CO_2 yields obtained in H_2SO_4-carbon reactions for a series of four carbons. These authors presented data for two activated carbons, and in both cases the ratio of CO_2 found to that calculated was between 0.7 and 0.8. By contrast, two coke samples gave values of 1.0 and 1.2. These results, like those reported above for this investigation suggest that good sorbents adsorb SO_2 reversibly and give lower CO_2:SO_2 ratios on thermal desorption than that postulated by the carbon-sulfuric acid reaction.

The relatively large CO_2 evolution at the low and high temperature regions of the desorption cycle occurs at temperatures where SO_2 evolution is minimal and cannot be attributed to reversible adsorption. These undoubtedly are associated with the reaction of oxygen and surface oxides with carbon at the sorption and desorption temperatures.

At ambient temperatures, a low surface concentration of groups having the characteristics of hydroperoxides has been reported during air oxidation of coals.[68] Jones and Townsend[66] claim that the initial reaction of both coal and active carbon with oxygen appears to involve chemisorption followed in the presence of water by the formation of a complex of oxygen and water having the oxidizing properties of peroxygen. This peroxygen complex was quite stable up to 70°C and was not completely destroyed until 350°C was reached. Oxidation above 70°C resulted in an increase in both the proportion of carbon dioxide to carbon monoxide produced and in the amount of oxygen fixed by the coal in acidic groupings. Jones and Townsend substantiated these observations by means of gravimetric balances for the coal-oxygen reaction at 50°C to 90°C. It is most probable that the appearance of relatively large amounts of CO_2 at the low and high desorption temperatures is due to the decomposition of complexes formed by reaction of the active carbon with water and oxygen in the synthetic flue gas. Friedman and Kinney[67] reported the evolution of CO_2 when air was bled through coal and active carbon beds at temperatures as low as 150°C. Lowry[68] mentions the decarboxylation of humic acids formed by air oxidation of coal at temperatures below 175°C. Thus, there is ample evidence that oxygen reacts with coal and active carbons to form materials which decompose to CO_2 on heating in the temperature ranges studied.

Although the MS and VPC studies both indicated some reduction in the SO_2 desorption temperature when hydrogen was used in place of an inert gas, the degree of improvement was too small to be significant in the operation of a carbon sorbing system. Moreover, the entire carbon picture may have changed since the inception of this work. Chemiebau, who now market the Reinluft Process, claim to have made changes, described above, which eliminated the fires that consumed the carbon sorbent bed after relatively short operating periods. If this is true, there is little incentive for seeking a gaseous reduction system to reduce adsorbed SO_x or H_2SO_4, since the coke itself is a lower cost reductant than either H_2 or CO, and reduction of SO_x with coke eliminates the capital costs associated with heating and handling a reducing gas.

SECTION IV - EVALUATION OF POTENTIAL SO_2 SORPTION SYSTEMS

The two best sorbents evaluated were sodium carbonate and copper on silica-alumina.

Sodium carbonate has good sorbent properties, is stable and inexpensive. It is an effective sorbent at stack gas temperatures and could be operated such that separation of fly ash from the stack gases could be made a part of a sodium carbonate recovery system.

Because copper on silica alumina is an effective sorbent only at 350-400°C, a sorber using this material would have to be located between the boiler and the air preheater. This restricts the use of this system to new plants in which such a sorber system could be designed. The copper on silica-alumina systems could probably be operated in fluid beds. Regeneration of the sorbent is achieved by merely increasing the sorbent temperature by about 100-150°C. Unfortunately, a relatively long regeneration time is required. Both systems were evaluated, as described below.

A. REGENERATION OF NA_2CO_3 BY THE MODIFIED LeBLANC PROCESS

Although the sorptivities noted in Table VIII, page 43 for SO_2 were far higher than those noted with other sorbents, sodium carbonate could not be considered in any sorption process that was not regenerative. The first regeneration system considered was similar to the LeBlanc Na_2CO_3 process and was as follows:

$$4Na_2SO_3 \xrightarrow{\text{Heat}} 3Na_2SO_4 + Na_2S \qquad (1)$$

$$3Na_2SO_4 + 6C \rightarrow 3Na_2S + 6CO_2 \qquad (2)$$

$$4Na_2S + 4CaCO_3 \rightarrow 4Na_2CO_3 + 4CaS \qquad (3)$$

Reaction (1) forming Na_2SO_4 occurs at temperatures above 600°C. Sodium sulfate can be reduced with coal or coke to sodium sulfide with the evolution of CO_2 (2) and the sodium sulfide can react with calcium carbonate to form sodium carbonate and calcium sulfide (3).

All these reactions require high temperatures and could probably be conducted in a single reactor. Thus, the spent sodium sulfite would be mixed with coal or coke and calcium carbonate, and the product sodium carbonate would be extracted from the CaS and unreacted coke and re-crystallized. Crystallization could be varied to optimize surface properties and form an active sodium carbonate. It might be desirable to add some of the CO_2 evolved during regeneration to the aqueous sodium carbonate solution to form some sodium bicarbonate, since the presence of sodium bicarbonate definitely favors increased SO_2 sorption.

The calcium sulfide can be converted to calcium carbonate and hydrogen sulfide by the Chance-Claus reaction with CO_2 in water at about 90°C, or 190°F, according to the following reaction:

$$CaS + CO_2 + H_2O \xrightarrow{90°C} CaCO_3 + H_2S$$

This reaction has been studied at FMC under the Office of Coal Research's Char Oil Energy Development program (Project COED), and streams having as much as 20% hydrogen sulfide in CO_2 were recovered from the calcium sulfide. The regenerated calcium carbonate would then be recycled to the sodium carbonate regenerator.

The flow sheet for this process is shown in Figure 11. The sodium carbonate reacts with SO_2, is collected in a bag filter, and is mixed with coal and calcium carbonate. The reactants pass to a rotary kiln where the Na_2CO_3 regeneration reactions are carried out. The reactivated sodium carbonate is dissolved in water to separate it from the calcium sulfide and crystallized. Residual fly ash that may be trapped with the sodium sulfite would also be removed in the sodium carbonate extractor. The calcium sulfide is converted to the carbonate. This processing scheme makes no solid waste products and produces hydrogen sulfide, from which sulfur can readily be obtained.

The reactions employed in this regeneration concept were explored briefly just before work on this contract was terminated in studies that are summarized on pages 1 and 2 in Appendix III. In runs made at 1000°C and 1200°C, the yield of sodium carbonate was only 11-17% of theory. An additional 25-40 weight percent of the sodium charged was recovered as sodium sulfide.

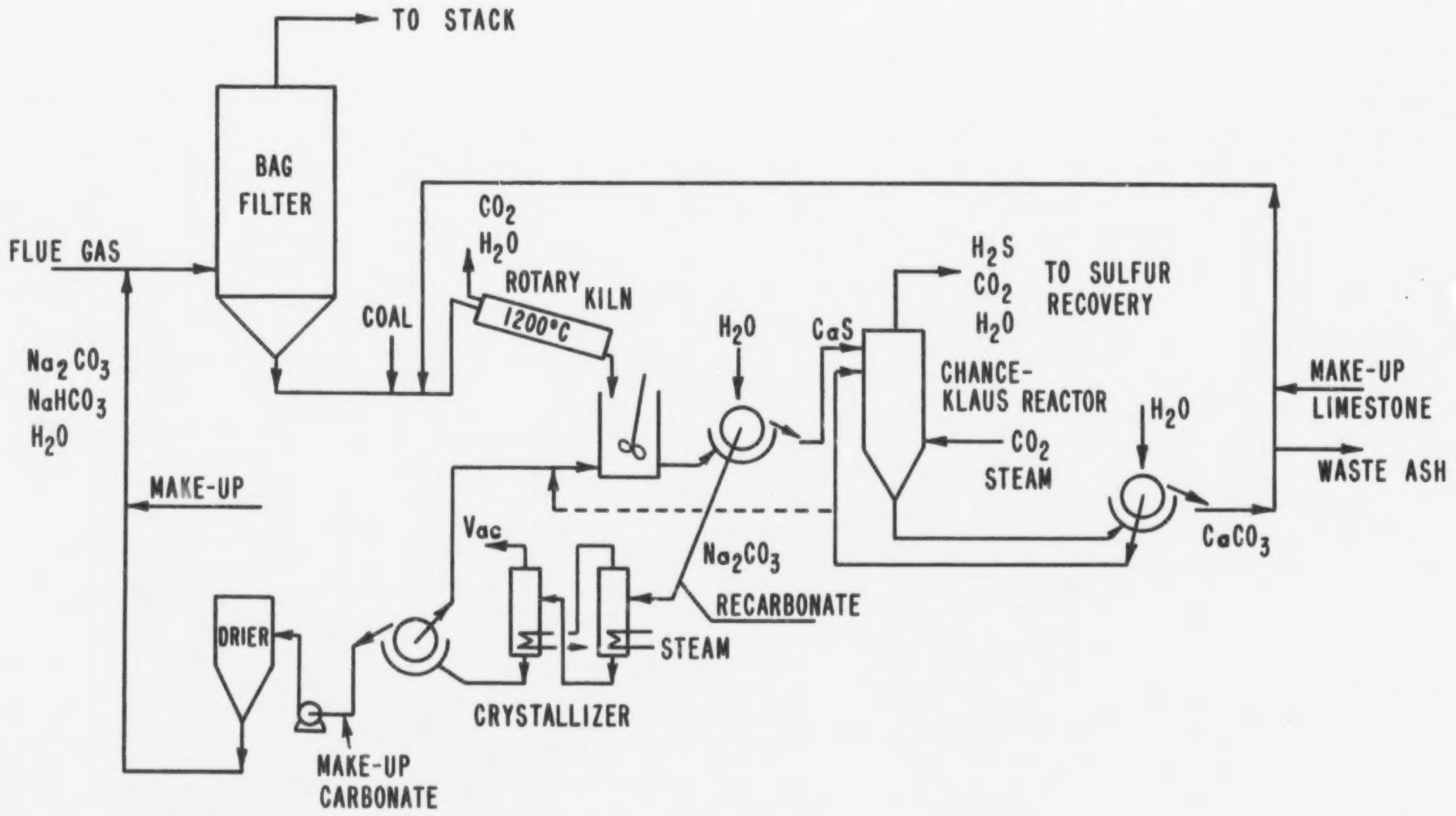

TO STACK
BAG FILTER
FLUE GAS
Na_2CO_3
$NaHCO_3$
H_2O
MAKE-UP
DRIER
MAKE-UP CARBONATE
COAL
CO_2
H_2O
ROTARY KILN
1200°C
V_{ac}
CRYSTALLIZER
STEAM
Na_2CO_3
RECARBONATE
H_2O
CaS
H_2S
CO_2
H_2O
TO SULFUR RECOVERY
CHANCE-KLAUS REACTOR
CO_2
STEAM
H_2O
$CaCO_3$
MAKE-UP LIMESTONE
WASTE ASH

FIGURE 11 - REMOVAL OF SO_2 FROM FLUE GAS WITH SODIUM SESQUI-CARBONATE AND REGENERATION OF THE SORBENT BY A MODIFIED LEBLANC PROCESS

The reaction of sodium sulfide with calcium carbonate can occur only after the sodium sulfite or sulfate has been reduced to the sulfide. However, at temperatures at which the reduction of sodium sulfate with coal occurs, calcium carbonate decomposes to calcium oxide and CO_2. Since the decomposition of calcium carbonate proceeds faster than the reduction reaction, little calcium carbonate apparently was available to react with sodium sulfide. This was partially confirmed by the fact that when sodium sulfide was reacted with calcium carbonate and coal under the same conditions, substantially higher yields of sodium carbonate resulted (43-47%).

The use of a nitrogen sweep gas in these experiments may also have contributed to the low Na_2CO_3 yields. Some recent Russian work[59] suggests that the type of carbon used markedly affects the reaction rate but that the first reaction probably is formation of carbon monoxide which reduces the sodium sulfate. The use of a nitrogen sweep gas would remove CO from the system and tend to give lower yields.

Design calculation showed that 205,000 pounds of sodium carbonate had to be regenerated each hour for an 800 mw power plant. This necessitated the use of regeneration reactions that were relatively rapid. Because our results and those in the literature failed to offer much encouragement for the development of short regeneration times under the modified LeBlanc process outlined above, a second regeneration system was considered.

B. REGENERATION OF SODIUM CARBONATE BY CARBON-CO_2 OR HYDROGEN-CO_2 REACTIONS

The second sodium carbonate regeneration system considered was based on the following two reactions:

$$2Na_2SO_3 + 3C \rightarrow 2Na_2S + 3CO_2 \qquad (1)$$

$$Na_2S + CO_2 \xrightarrow{H_2O} Na_2CO_3 + H_2S \qquad (2)$$

The carbonation of sodium sulfide shown in reaction (2) was tested in the lab and found to proceed very rapidly (see Appendix III, pages 5-7). Therefore, attention was given to the first reaction which involved the reduction of sodium sulfite to sodium sulfide with either carbon or hydrogen.

Fotiev[60] reported that on reduction with carbon, sodium sulfite was reduced to the sodium sulfide in 70% yield in 10 minutes at 600°C, and a conversion of 84.5% in two minutes was reported for reduction at 700°C. Puttagunta[61] reported that sodium sulfite could be reduced by hydrogen at 677°C in 79 to 89% yield in as little as 5 minutes using an iron oxide catalyst. Pollyvyannyi[62] reported the reduction of sodium sulfate with carbon monoxide to sodium sulfite in 97% to 99% yields in 10 to 15 minutes at 1000°C. Thus, there was ample evidence in the literature to support the concept of rapid reduction of sodium sulfite or sodium sulfate to sodium sulfide.

Kirk and Othmer[63] noted that sodium sulfide is now being made in Germany by the reduction of sodium sulfate with hydrogen at 600°C in a brick lined rotary kiln using fine iron oxide catalyst. In this system the reaction is carried out continuously at a lower temperature and with less corrosion than with carbon reduction. The yield of Na_2S obtained is said to be over 95% but no reaction time is cited.

In their progress report #2, Atomic International described a process which used hydrogen at 600°C under a pressure of 10 atmospheres and an iron catalyst to reduce sodium sulfite and sodium sulfate to sodium sulfide in 40 minutes.[64] They also reported that the reduction could be done in a fluidized coke bed at 800°C and 1 atmosphere with the same iron catalyst and a 16 minute reaction time.

The reduction of sodium sulfite to sodium sulfide with carbon was studied briefly, as described in the Appendix III, pages 2 and 3. Sodium sulfide was obtained in 47% yield after 1 hour at 1000°C. Other temperatures were not tried. The literature cited above suggests that this probably was too high a reaction temperature, but it was used to make the results comparable with those obtained with the calcium carbonate-carbon runs described above to compare the relative product yields in the different processes.

Another regeneration system considered used the same two stage concept in which the sulfite or sulfate was reduced to the sulfide and was then carbonated, but used hydrogen instead of carbon for the reduction. Both flow sheets are shown in Figures 12 and 13, and are discussed below.

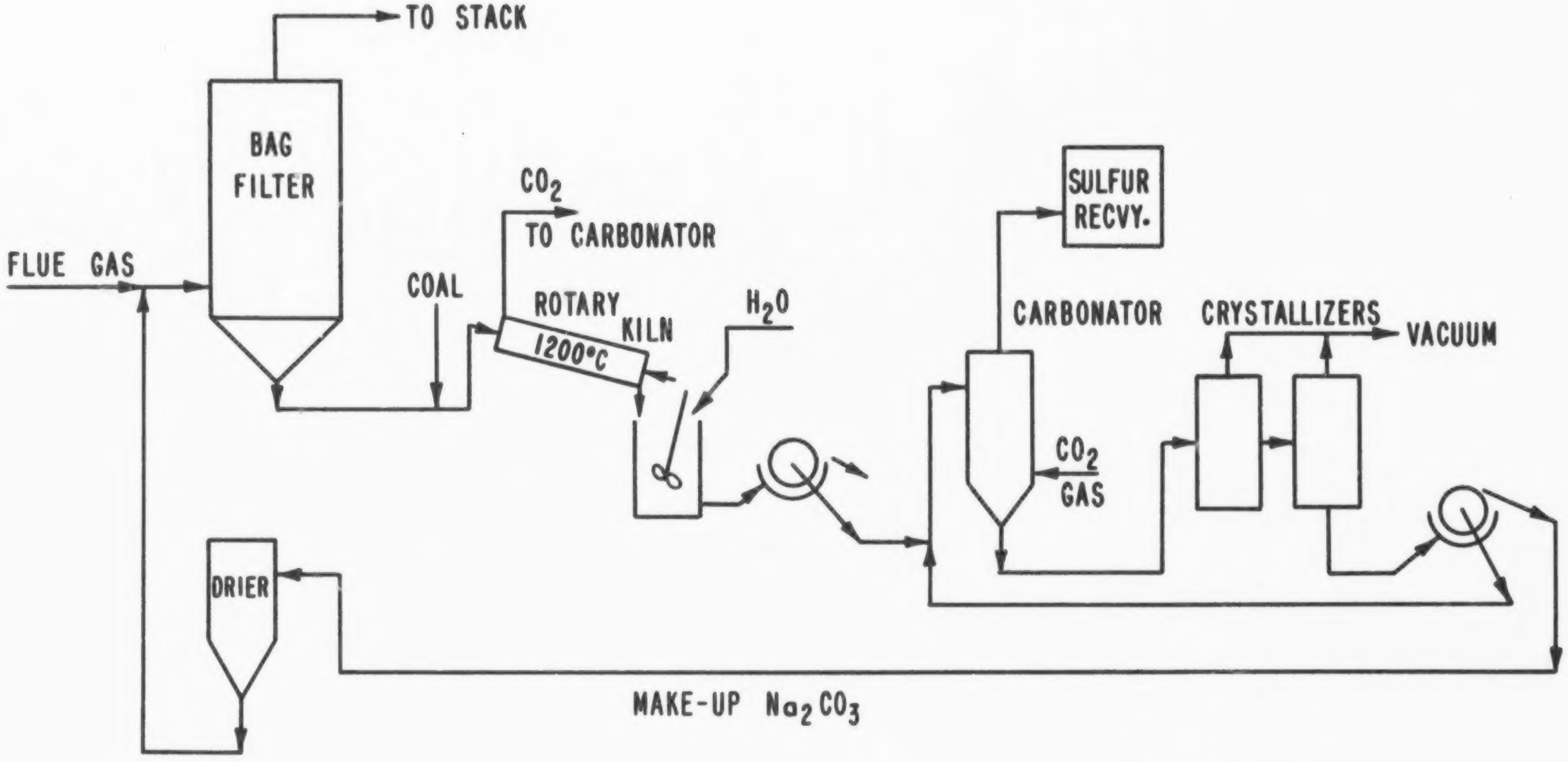

TO STACK
BAG FILTER
FLUE GAS
COAL
CO_2 TO CARBONATOR
ROTARY KILN
1200°C
H_2O
SULFUR RECVY.
CARBONATOR
CO_2 GAS
CRYSTALLIZERS
VACUUM
DRIER
MAKE-UP Na_2CO_3

FIGURE 12–TWO-STAGE Na_2CO_3 REGENERATION PROCESS
(1) REDUCTION OF Na_2SO_3 WITH COAL
(2) CARBONATION OF Na_2S SOLUTION

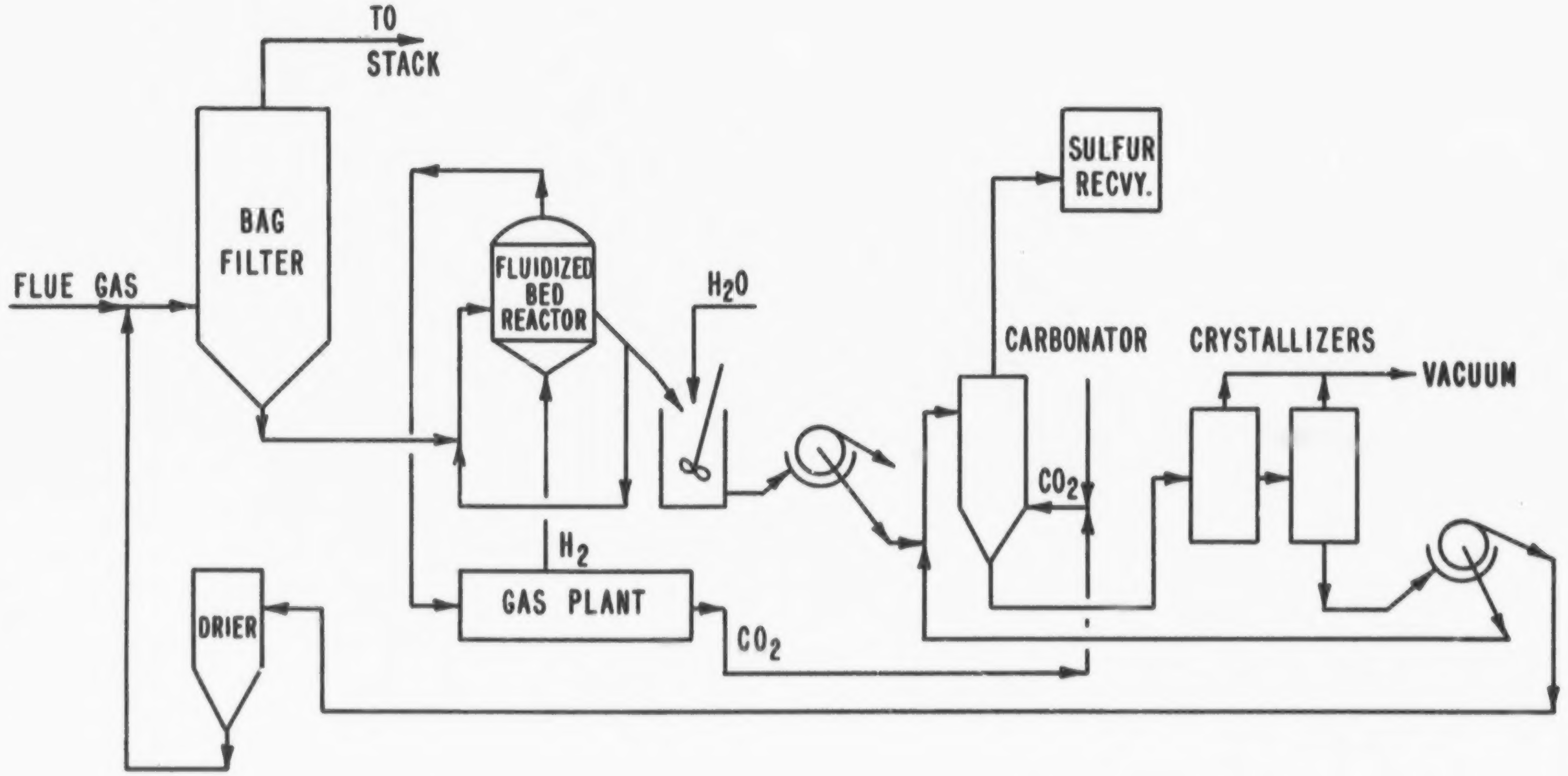

TO
STACK
BAG
FILTER
FLUE GAS
FLUIDIZED
BED
REACTOR
H_2O
SULFUR
RECVY.
CARBONATOR
CRYSTALLIZERS
VACUUM
CO_2
H_2
GAS PLANT
CO_2
DRIER

FIGURE 13 - TWO-STAGE Na_2CO_3 REGENERATION PROCESS

(1) REDUCTION OF Na_2SO_3 WITH H_2
(2) CARBONATION OF Na_2S SOLUTION

1. Economic Evaluation of the Na_2CO_3 Regeneration Process

An economic evaluation was made for the sodium carbonate regeneration scheme shown in Figure 12.

In this flow sheet, sodium carbonate is blown into the flue duct to trap SO_2 and the flue gas passes through a bag filter. The SO_2-free gas escapes to the atmosphere and the sodium carbonate is retained in thin layers on the bag filters. After a section of the bag filter has been spent, the sodium carbonate is knocked off the bag and is blown to the regenerator.

In this sketch, the regenerator is a brick-lined kiln in which coal is used to reduce the sodium sulfite. The reduced sodium sulfite goes to a water tank where it is slurried. The fly ash collected with the Na_2CO_3 in the bag filters is filtered from the soluble sodium sulfide and the sodium sulfite solution is then carbonated with CO_2. The CO_2-H_2S mixture leaving the carbonator goes to H_2S recovery and the sodium carbonate solution goes to multi-stage evaporators where water is removed. The sodium carbonate crystals are recovered by centrifuging, dried, and returned to the sodium carbonate storage tank.

The bag filter sorber is composed of 24 cells, 16 x 16 x 40 ft. and has filter bags having 364,000 ft^2 of surface area. The rotary kiln used to reduce the sodium sulfite is 16 ft in diameter, 600 ft long, and has a brick lining. The dissolving tanks for the sodium sulfide have 50,000 gallons capacity, and it is assumed that two would handle the flow. The carbonation tower is 42 ft in diameter and 30 ft high.

The estimated capital cost for the equipment* is summarized in Table XXXIX. Direct plant costs for an 800 mw plant amount to $22,484,000. Adding the cost of the sulfur recovery plant and construction items brings the total construction costs to $38MM.

The operating costs for this plant are shown in Table XL. The cost factors used are the same as those used

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*The list of equipment needed and their estimated costs are presented in Appendix IV.

TABLE XXXIX

Direct Plant Costs for a Na_2CO_3 Regeneration System Using Carbon Reduction of Na_2SO_3 and Carbonation of the Resultant Na_2S

	% of Equip. Costs	Material	Labor	Total
Excavation + Site Prep.	8	$ 75,000	$ 700,000	$ 775,000
Concrete + Foundations	15	460,000	1,000,000	1,460,000
Structures + Buildings	35	2,200,000	1,200,000	3,400,000
Machinery + Equipment	100	9,555,870	1,250,000	10,805,870
Piping	15	660,000	800,000	1,460,000
Electrical	22	700,000	1,440,000	2,140,000
Instruments	17	450,000	1,200,000	1,650,000
Paint + Scaffolding	5	86,000	400,000	486,000
Insulation	3	205,000	102,500	307,500
	220	14,391,870	8,092,500	22,484,370
Direct Plant Cost		14,391,870	8,092,500	22,484,370
Sulfur Recovery Plant 200 t/d				2,620,000
Engineering 18% Direct				4,050,000
Indirect 20%				4,500,000
Contingency 20%				4,500,000
Construction Costs				38,154,370
				$47.50/kw

TABLE XL

Operating Cost for a Na_2CO_3 Regeneration System using Carbon Reduction of Na_2SO_3 and Carbonation of the Resultant Na_2S

Capital Charges	14% Inv.	5,330,000
Maintenance	5% Inv.	1,910,000
Labor 3 day + 7 m/s	@ $3/hr + Sup. @ $12,000/yr	202,000
Payroll OH	40% L	81,000
Plant OH	50% M & L	1,106,000
Make-Up Sesqui	$30/T	1,600,000
Coal	$4.20/T	840,000
Power	$0.004/kwh	152,000
Water	$0.10/1000 gal.	72,000
Steam	$0.50/1000 lb	180,000
	OPERATING COST	11,473,000
Sulfur Credit	72,000 T/y @ 14	1,000,000
Credit for Precipitator		651,200
Net Desulfurizing Cost		9,821,800

Cost/Ton Coal 800 mw = 2.6 MM T/Y	$3.78/Ton
Cost/Ton Sulfur removed	
No credit for sulfur	$150
With sulfur credit	$137

by Esso Research and Engineering in their report to NAPCA on Contract PH-86-67-130 dated August 27, 1969.[71] Capital related charges have been estimated at 14% of the investment and maintenance at 5%. The annual operating costs for capital charges, labor, and utilities amounts to slightly less than $11.5MM. Based on a $14/ton price, a sulfur credit of $1MM was taken for the 72,000 tons of sulfur credit. Taking this plus an additional credit for the elimination of the electrostatic precipitators, the net cost of removing SO_2 from flue gas is about $3.75 per ton of coal.

Although it was not evaluated in detail, preliminary estimates indicated that the hydrogen reduction shown in Figure 13 would be considerably more expensive than coal reduction. To make the process operable, the hydrogen has to be heated to 2200°F in order to have enough sensible heat to raise the sodium carbonate to the reduction temperature. The wet hydrogen has to be cooled to remove the large amount of water formed by the reduction of sodium sulfite, and the hydrogen has to be reheated to 2200°F. Because of the cost of the very large heat exchangers required to heat the hydrogen to over 2000°F and because the cost of the hydrogen needed to reduce the sodium sulfite is nearly three times* that of the coal required for the same reduction, the hydrogen reduction system was considerably more expensive than the system shown. Therefore, the economic evaluation using hydrogen reduction was not completed.

An examination of the capital charges for this process did not reveal any single area in which large savings might result through improvement in technology. The high capital costs result from the need for many pieces of equipment to handle a large mass of material, and the large heat requirements.

One major cost reducing approach is suggested by the work of Gorbanev[69], who reduced Na_2SO_4 to Na_2CO_3 with a gas consisting of 20% H_2, 20% CO, and 60% N_2 at about 670°C. This gas was made by reacting steam together with air in a gas producer. Gorbanev's main reaction probably was

$$Na_2SO_4 + 2H_2 + 2CO = Na_2CO_3 + H_2S + CO_2 \quad H_2O$$

and he reported 95-97% conversion in eight hours.

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*The hydrogen cost was estimated at 25¢/Mcf, coal at $4.20/Ton.

Gorbanev's system has certain potential advantages: (1) it uses an inexpensive gas which can be produced at the 600-700°F reduction temperature, (2) the reaction might be carried out in a fluidized bed reactor, and (3) the conversion reaction occurs in the solid state, so that no dissolving and recrystallization reactions are involved. These offer a major potential for lower capital and power costs than those cited above.

The major drawback to this system is its relatively long reaction time. However, the literature cited above indicates that Na_2SO_3 is reduced with carbon or H_2 much more readily than Na_2SO_4. If a similar increase in reduction rate is obtained with Gorbanev's gas reaction, sodium carbonate regeneration times for this process may also be reduced very significantly.

C. COPPER-IMPREGNATED SORBENTS

1. Sorption

a. On S-46 Silica Alumina

Several series of runs were made to study the sorption potential of copper-impregnated silica-aluminas for removing SO_2 from synthetic flue gas mixtures after the screening studies described above showed that such preparations sorbed over 16 weight percent of SO_2.

Table XLI shows how the sorptive capacity for copper impregnated S-46 silica alumina increased as the sorptive temperatures were raised from 150° to 400°C. Copper-impregnated materials only sorb appreciable amounts of SO_2 at or above 350°C where copper's Redox activity manifests itself.

TABLE XLI

Effect of Temperature on Sorptive Properties of Copper-Impregnated Houdry S-46 Silica-Alumina

Sample No.	% Cu	Sorption Temp., °C	SO_2 Sorbed, Wt. %
T21-13	6.63	150	0.3
		250	1.5
		350	6.1
		400	7.5
T21-16	7.7	250	1.0
		400	8.6
T21-15	11.3	150	0.2
		250	2.8
		400	19.8

Table XLII shows the sorption-desorption cycling behavior of copper-impregnated S-46 silica alumina containing 11.3 to 11.6 weight percent copper. The materials were reduced with hydrogen overnight and were evaluated during the next day, then the regeneration was repeated during the next night. Because of the relatively long times required for these runs, these sorptions were monitored by iodine titration in order not to tie up the screening units. The sorptions were stopped when 80% breakthrough of the SO_2 was recorded for 3 consecutive 2-minute intervals. These data show that 400°C was somewhat more effective than 350°C and that in the three cycles studied there was no loss of SO_2 sorption activity.

TABLE XLII

Sorption-Desorption Cycling of Copper-Impregnated S-46 Silica-Alumina

Reducing Gas - H_2 @ 550°C

		T21-15[a]		T21-24[b]
Sorption Temp. °C		350	400	400
Cycle No.	1	9.6	14.2	12.7
	2	12.4	15.4	14.8
	3	10.6	16.6	15.1

[a] 11.3% Cu

[b] 11.6% Cu

b. On Other Silica-Aluminas

The studies described above were all made with Houdry Process and Chemical Company S-46 silica-alumina. Other silica-aluminas were obtained from Houdry to determine whether these produced more active copper-impregnated sorbents. The physical and chemical properties of the silica-alumina samples tested are shown in Table XLIII and the results obtained from their evaluation are shown in Table XLIV.

TABLE XLIII

Physical and Chemical Properties of Experimental Silica-Alumina Samples

Houdry Type No.	S-65	S-46	S-34	S-16
Physical Properties				
Surface Area, m^2/g	375-400	290-315	180-200	80
Packed Bulk Density, kg/l	0.54	0.62	0.63	0.66
Pellet Density, gm/cc	0.86	0.99	1.02	1.24
Porosity, Vol. %	60	57	56	47
Absorption, Wt. %	65	58	55	38
Real Density, gm/cc	2.2 - 2.4			
Avg. Pore Diameter, A°	80	82	85	380
Chemical Properties				
Al_2O_3, Wt. %*	12.4			
SiO_2, Wt. %*	87.3			
Na_2O, Wt. %*	0.25			

*Ignited Basis

TABLE XLIV

Sorption of SO_2 on Copper-Impregnated Houdry S-46 Silica-Alumina @ 400°C

Sample No.	Surface Area m^2/g	% Cu	SO_2 Sorbed g/100 g Sorbent @ 80% Breakthrough
T21-22	80	12.99	6.5
T21-23	180-200	12.40	7.7
T21-24	290-315	12.70	11.3, 13.2
T21-25	375-400	13.32	10.9, 10.8
T21-27	80	7.9	4.6
T21-28	180-200	8.2	4.5
T21-30	290-315	9.6	7.7
T21-32	290-315	7.9	6.0, 6.1

Sorption of SO_2 on copper-impregnated silica-aluminas increases with surface area up to a maximum of about 300 m^2/g. These data, like those presented in Table XLI, showed that silica-alumina impregnated with 12% copper was a more active SO_2 sorbent than one impregnated with 8% copper. The amount of SO_2 sorbed on the T21-24 silica-alumina impregnated with 12% copper is the stoichiometric amount calculated for the reaction between copper and SO_2.

c. On Miscellaneous Materials

To obtain a cost figure for the silica-alumina used in the copper on silica-alumina sorbents, Houdry Processing Chemical Company and Mobil Oil Company were contacted. Neither now markets silica-alumina cracking catalysts, since these have been supplanted entirely in petroleum cracking practice by the molecular sieve catalysts.

Houdry offered to supply the silica-alumina catalyst if markets for sufficiently large volume existed, and agreed that the amount required for a 1000 mw plant would qualify on this respect. Houdry's quoted price for a bead S-46 type catalyst is 40¢/lb. The use of a bead as opposed to a pelleted catalyst probably would make no difference in these studies, assuming that the surface area would remain the same. However, the 40¢/pound quotation for a sorbent carrier prompted a study of the relative activities of other potential copper-supporting sorbents. Those investigated are shown in Table XLV. The ceramic foam and activated bauxite are relatively inexpensive, high-temperature resistant materials. The bead silica is 99% silica and was chosen because of its excellent thermal properties. The natural silica-alumina and zeolites were selected because these were much cheaper than the synthetic materials which were shown previously to be good supports.

The bead silica was a good sorbent but its cost of approximately $1/lb would rule out its use in an SO_2 sorbing system. The activated bauxite which sells for approximately 7¢/lb was an excellent sorbent; sample T21-37 showed sorptive capacity equivalent to that obtained with impregnated silica-alumina. This is the lowest cost material found which was a good support for copper-based materials. However, the activated bauxite may not be able to withstand repeated regeneration at 500 to 550°C, since it might change to the boehmite form which has a lower surface area and might be a poorer sorbent. This was not checked.

TABLE XLV

Sorption of SO_2 on Miscellaneous Copper-Impregnated Materials @ 400°C

Sample No.	Sample Type	Surface Area m^2/g	Copper g/100g Sorbent	SO_2 Sorbed g/100g Sorbent
T21-26	Ceramic Foam	2	12.2	5.8
T21-31	Ceramic Foam	2	9.1	3.2
T21-33	Silica Beads	350	12.1	12.5
T21-34	Silica Beads	350	7.2	6.5
T21-38	Natural SiO - Al_2O_3	100	11.2	4.5
T21-41	Natural SiO - Al_2O_3	100	8.1	4.9
T21-39	Natural Zeolite	130-140	12.5	5.2
T21-42	Natural Zeolite	130-140	7.8	4.9
T21-37	Activated Bauxite	-	11.2	14.1
T21-40	Activated Bauxite	-	7.0	9.8
T21-18	200 Al_2O_3	200	12.1	10.5
T21-19	200 Al_2O_3	200	8.1	9.4
T21-20	100 Al_2O_3	100	12.0	6.0
T21-21	100 Al_2O_3	100	7.6	3.6

The ceramic foam, natural silica-alumina and zeolite were all relatively poor SO_2 sorbents.

Another potential support for copper-based sorbents is alumina. Two batches of Houdry aluminas differing only in surface areas, were evaluated. As noted in Table XLV, the alumina with the larger surface area was a more effective copper support than that with the smaller surface area. The 200 alumina was not quite as effective as the activated bauxite when impregnated with approximately 12 weight percent copper. With alumina, reduction with hydrogen usually gave a product which sorbed 1 to 2 weight percent less SO_2 than did reduction with a hydrocarbon gas. The reason for this is unknown.

2. Desorption

a. Effect of Gas Composition on the Reduction of Copper-Impregnated Sorbents

The most active copper-impregnated sorbents were prepared by depositing copper nitrate on the support materials and reducing the nitrate to copper with a reducing gas. Unreduced copper nitrate was a poor sorbent for SO_2. To study how the compositions of the reducing gases affected the activity of copper-impregnated sorbents, several copper nitrate-impregnated materials were reduced with natural gas, hydrogen, and a mixture of 30% hydrogen, 20% CO, and 50% nitrogen, which simulated a producer gas. The use of producer gas would be particularly desirable, since it can be made at relatively low cost and hot producer gas could be passed directly into the sorbent bed to provide the temperature needed for the reduction. Sulfur cleanup for the gas would not be necessary, since any sulfur in the producer gas would be removed by the sorbent.

As seen in the data on Table XLVI, hydrogen and methane gave equivalent activation of sorbents. Producer gas was somewhat less effective when it was used with good sorbents, such as T21-24 and T21-33. However, with a relatively poor sorbent such as T21-26, producer gas was nearly as effective as hydrogen. Nitrogen, which does not reduce copper, was not an effective activating material.

TABLE XLVI

Effect of Reducing Gas Composition on Activity of Resulting Copper-Impregnated Sorbents

Sample No.	Sorbent Composition	Reducing Gas Composition	SO_2 Sorbed g/100g Sorbent
T21-23	12.4% Cu on 200 m^2/g SiO_2-Al_2O_3	Methane	8.0
		Hydrogen	7.7
T21-24	12.7% Cu on 300 m^2/g SiO_2-Al_2O_3	30% H_2, 20% CO 50% N_2	9.0
		Methane	11.3
		Hydrogen	13.2
T21-25	13.3% Cu on 400 m^2/g SiO_2-Al_2O_3	Methane	10.9
		Hydrogen	10.8
T21-26	12.2% Cu on Ceramic Foam	Nitrogen	2.2
		30% H_2, 20% CO 50% N_2	5.1
		Hydrogen	5.8
T21-27	7.5% Cu on 80 m^2/g SiO_2-Al_2O_3	Methane	4.6
		Hydrogen	4.1
T21-33	12.1% Cu on Silica Beads	30% H_2, 20% CO 50% N_2	9.3
		Hydrogen	12.5

b. Recovery of Sulfur on Desorption of SO_2 From Copper-Impregnated Silica-Alumina

A study was initiated to determine the form in which adsorbed SO_2 was removed from copper-impregnated silica-alumina sorbents. Studies conducted in the TGA apparatus by Tracor[75] had indicated that most of the sulfur recovered by thermal regeneration of copper sulfite and copper sulfate was evolved as SO_3.

The technique used to determine the form in which sulfur was evolved from the copper-impregnated silica-alumina sorbents is described in Appendix V. It consists of sorbing the SO_3 in aqueous isopropyl alcohol, trapping the hydrogen sulfide in cadmium acetate solution, and titrating the SO_2 in alkaline iodine solution.

Results for SO_2 and H_2S evolution at 450°C, 550°C, and 695°C are shown in Table XLVII. The bulk of the sulfur was evolved in the first hour and most was evolved as SO_2 rather than as H_2S. However, the fraction of sulfur recovered as H_2S increased as the temperatures were raised.

There are several possible explanations for the increased H_2S evolution with temperature. Higher temperature may favor the reaction of SO_2 with hydrogen to form H_2S and water, a reaction that is thermodynamically feasible throughout the temperature range studied.

Another possibility is that the hydrogen sulfide forms by a secondary reaction involving reduction of copper sulfide. The literature indicates that when copper nitrate is reduced with hydrogen or other reducing gas, the copper is converted to copper metal, copper sulfide, and copper oxide.[39] The relative amounts depend on the reducing conditions. Copper sulfides would be reduced with hydrogen to H_2S and copper. The fact that more hydrogen sulfide formed later in the reduction cycle would support the view that the hydrogen sulfide results largely from reduction of copper sulfide.

In both of these mechanisms, hydrogen is required for the formation of hydrogen sulfide. Replacing H_2 with natural gas would eliminate the two reactions postulated for hydrogen above; and if these mechanisms are responsible for the formation of hydrogen sulfide, none should form when methane is used as a reductant. Such was the case in a five hour reduction using methane as the reductant at 550°C; no hydrogen sulfide was found.

TABLE XLVII

Regeneration of Copper-Impregnated Silica-Alumina with Hydrogen

Temp., °C	450	550	695
SO_2 Evolved, mg			
0 - 1 hours	73.0	82.9	98.6
2 - 3 hours	12.1	4.2	5.8
4 - 5 hours	5.1	5.6	6.7
TOTAL	90.2	92.7	111.1
H_2S Evolved, mg			
0 - 1 hours	1.2	1.1	21.7
2 - 3 hours	2.4	5.9	15.7
4 - 5 hours	2.0	5.3	7.6
TOTAL	5.6	12.3	45.0
Mol Ratio Sulfur Recovered SO_2:H_2S	8.6:1	3.7:1	1.3:1

If copper oxides form during regeneration with methane and are not reduced, the copper might lose its activity on repeated sorption-desorption cycles using methane as the reducing gas. This did not occur, since copper-impregnated samples reactivated with methane retained their activity through repeated sorption and desorption cycles. The reason may be either that the amount of residual copper oxide remaining after each run was relatively low or that the residual copper oxide reacted with SO_2 in the next sorption cycle.

3. Evaluation

The data described above showed that copper-impregnated materials were reasonably good sorbents for SO_2 at 350-400°C, and that the sorbents could be regenerated by a reducing gas at temperatures 100-150°C higher than those used during sorption. However, these studies provided little information on either the ultimate life expectancy of the sorbent or its ability to withstand attrition. Therefore, it was impossible to establish the type of system in which copper-impregnated sorbents might be used.

To evaluate the effectiveness of copper-impregnated sorbents, an attempt was made to simplify comparisons between the best solids studied in this program and those reported in other programs. The simplest type of sorption rate relation was used (gm SO_2 absorbed/minute) as calculated from the raw data.[75] Additionally, because other experimenters used different SO_2 concentration in the simulated flue gas, an adjusted rate was calculated. This rate is calculated as the raw rate divided by the volume percent SO_2 in the flue gas. The adjusted rate is probably a more accurate way of comparing data from several sources as it attempts to minimize the effect of different flue gas concentrations. However, higher SO_2 concentrations do favor higher sorption rates.

The FMC results on sodium carbonates and copper-impregnated sorbents were compared with the Avco and CERL[72,74] (as reported by Avco, pg. 95) alkalized alumina work in Table XLVIII.

From the adjusted rate data in the tables, one can qualitatively conclude that sodium carbonate may be a better sorbent than alkalized alumina due to the higher adjusted rates at the same loading. This was true for all types of sodium carbonate studied (natural ash, run 53; anhydro sesquicarbonate, run 56; and precipitator cake, run 57).

TABLE XLVIII

Comparisons of Sorption Rates of SO_2 for Various Sorbents

Sorbent Type & Run #	% SO_2 in Flue Gas	T (°C)	Final Loading gm/SO_2 gm/solids	(gm/min) Sorption Rate at Various Loadings Raw Values 5%	 10%	 20%	 Adjusted Values 5%	 10%	 20%
Natural Ash FMC #53	.35	125	.387	.0083	.0074	.0037	.024	.021	.011
Anhydrous Sesquicarbonate FMC #56	.35	125	.462	.0092	.0075	.0044	.026	.022	.013
Na_2CO_3 Precipitator Coke FMC #51	.35	125	.330	.0082	.0066	.0022	.023	.019	.006
11.3% Cu on Silica Alumina Run #63	.35	400	.185	.0055	.0025	-	.0016	.007	-
12.1% Cu on Bauxite Run #121	.35	400	.156	.0028	.0018	-	.008	.005	-
Alkalyzed Alumina Avco Run #S082	.92	300	.355	.020	.012	.0065	.022	.013	.007
CERL Alkalyzed Alumina reported by Avco pg. 95	.622	130	.24	.010	.0075	-	.016	.012	-

The copper runs show a lower rate of sorption than either the sodium carbonate or alkalyzed alumina at the same loadings. The copper runs also had the lowest final loadings.

The copper-impregnated sorbents fared poorly in this comparison because the sorption rates were calculated only up to 20% SO_2 breakthrough. Copper-impregnated materials normally show a faster 20 to 30% SO_2 breakthrough than either sodium carbonate or alkalized alumina, but the SO_2 breakthrough rate for copper-impregnated sorbents slows thereafter (see Table XVII, page 54). However, because the copper-impregnated sorbent made such a relatively poor showing in this comparison, more emphasis was given to the sodium carbonate evaluation, which was presented above.

A recent Bureau of Mines paper[76] estimated the cost of utilizing a copper oxide on alumina absorbent for removing SO_2 from flue gas at 1.62 mills/kwh or $4.62/ton of coal. The Bureau's sorbent, 6.5% copper on alumina, sorbed only 4% SO_2 which is consistent with results shown in Table XLV above. The Bureau's evaluation procedure was adapted to the 10-12% copper on silica-alumina described above which sorbed about 15% SO_2 in the screening test. The absorber regenerator size was conservatively cut in half, resulting in a 30% capital savings, and sorbent requirements were cut by 50%. Assuming the same utilities requirements and sorbent makeup rate as the Bureau, the operating cost for the copper on silica-alumina sorption process becomes 1.44 mills/kwh or $4.10/ton of coal. This is slightly higher than that shown above for the sodium carbonate regeneration process.

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APPENDIX I

COMPUTER PROGRAM OPERATION

Appendix I is a computer program for SO_2 sorption data reduction. These data were taken on a copper-on-alumina catalyst that was evaluated at 300°C with a synthetic flue gas flow of 1000 cc/min. through a one-gram sample. The cumulative SO_2 adsorption column shows a sorption of 5.58 weight percent SO_2 on the sorbent.

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TREATMENT OF DATA

The raw data from each experimental sorbent run is obtained as values of SO_2 concentration in the effluent gas stream versus time. A typical computer generated plot of these data is presented in Figure A for run No. 63.

DEAD TIME CORRECTION

The experimental system is of measurable volume, giving rise to some degree of holdup. Therefore, a residence time correction must be applied to the measured concentration-time data for each experimental run.

In order to calculate this correction, a series of experimental runs was made with an inert solid material and with the same gas mixture as in the active solids runs. As in the active solids runs, effluent concentration, C_B, and time were measured. One run with inert solids was made for each unique combination of flow-rate, temperature, and feed concentration. From these inert runs, a function was generated which would be used to correct the active solids runs for the system holdup.

In the figure below, the line labeled blank run represents one such dead time correction function. It was found that a quadratic function running through T_I, the last experimental point before breakthrough, fit rather well for the dead time correction. The quadratic function resulted in the top of the ramp at T_A being slightly to the left of what it really should be. However, the error involved is very small, not worth using a more complicated multiple-piece function.

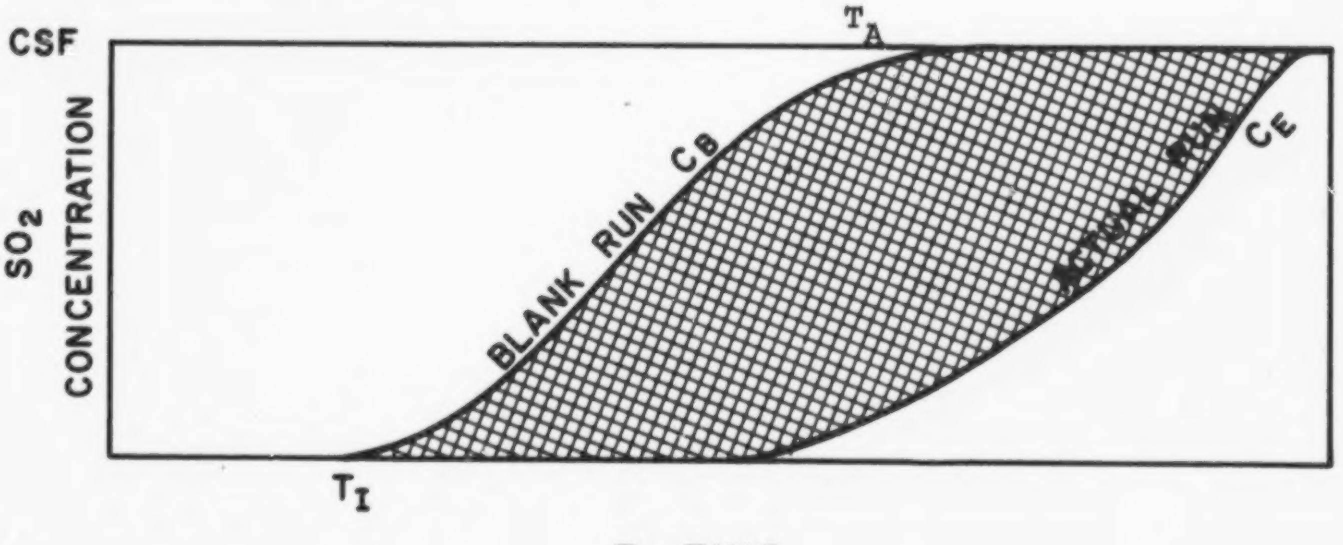
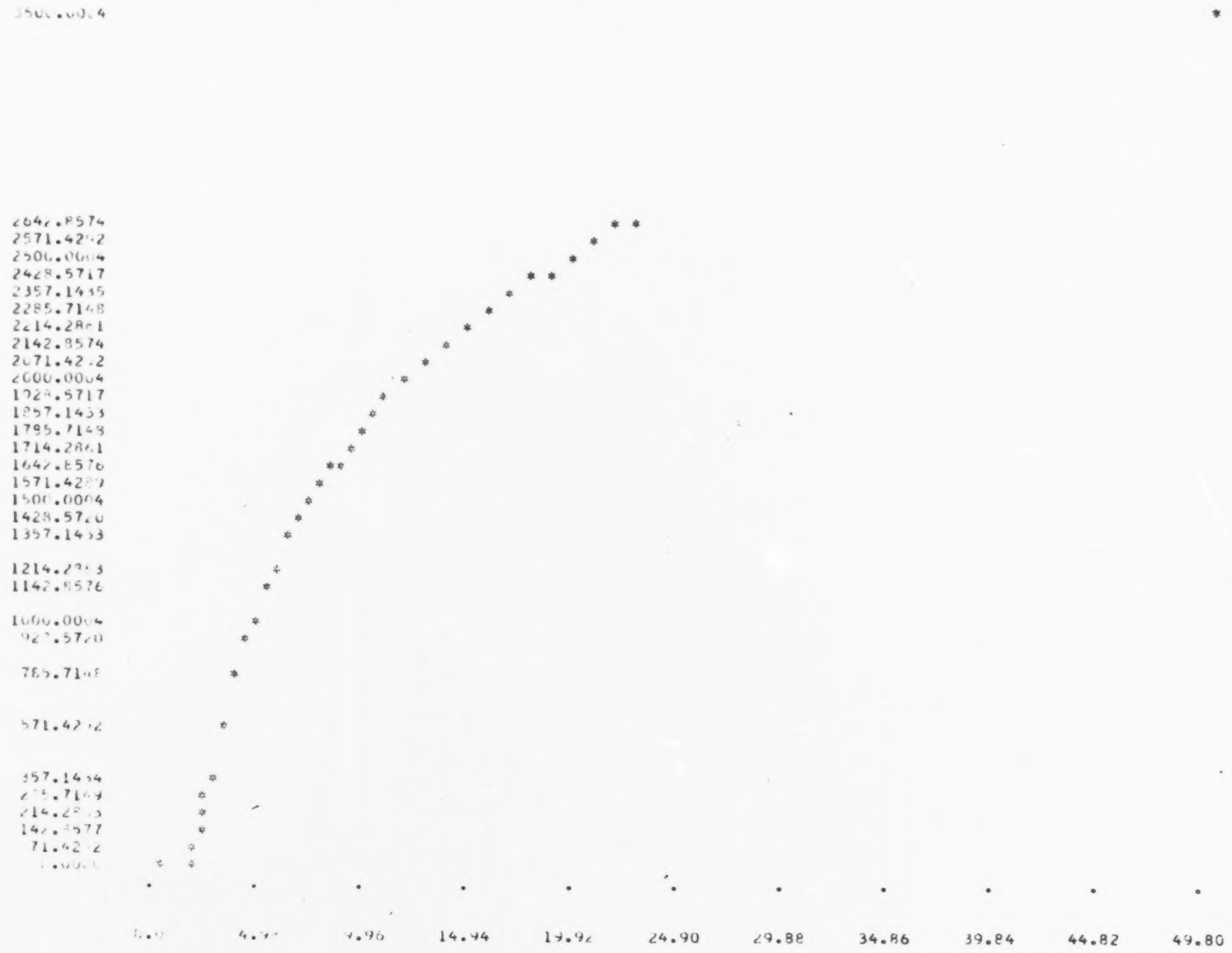


Figure B

Figure A

SORPTION CURVE
PLOT OF SO2 EXIT CONCENTRATION VS. TIME



CALCULATION OF SO_2 ABSORBED ON SOLID

In the figure above, C_B is the value of the dead time concentration function at any time, T, for an inert solids run. The line labeled actual run is the concentration time profile for an active sorbent run with C_E, the measured effluent concentration at time, T. The cross hatched area between the active sorbent profile and the dead time profile is used as the basis for calculating the amount of SO_2 sorbed.

The amount of SO_2 sorbed in any time period T_1 to T_2 is:

$$\text{Sorbed} = \text{FLOW}\left(\frac{\text{liters}}{\text{min.}}\right) \times \frac{64.}{22.4} \int_{T_1}^{T_2} (C_B - C_E)\, d(\text{TIME})$$

In our case since we are dealing with discrete measurements of C_E, C_B, and TIME, where I is the I'th measured data point, the amount sorbed up to TIME (I), W (I) is:

$$W(I) = \text{FLOW} \times \frac{64.}{22.4} \sum_{I=1}^{I} [C_B(I) - C_E(I)] \quad [\text{TIME}(I) - \text{TIME}(I-1)]$$

The instantaneous sorption rate at TIME(I), RI(I) is

$$RI(I) = \text{FLOW} \times \frac{64.}{22.4} \times [C_B(I) - C_E(I))]$$

CALCULATION OF FINAL SORPTIVE CAPACITY OF SOLID

Most experimental runs were stopped short of total saturation of the solid with SO_2 because of the lengthy time involved. Therefore, it was necessary to determine what the total sorptive capacity of the solid would be if the experiments had proceeded to conclusion. This was done by extrapolating the instantaneous sorption rate to zero and measuring the SO_2 sorbed up to that point.

Let SADE denote the SO_2 sorbed from the beginning of run to the end of measurements (call this time TIML); the instantaneous rate at this time call RIL.

Using the last five measured data points, fit RI vs. TIMF using a quadratic relationship, and calculate the constants A, B, and C for

$$\text{TIME} = C + B \times RI + A \times RI \times RI$$

The time at which the rate of sorption is zero is then equal to C and is denoted as TIMF. Figure C shows this extrapolation graphically.

Having found TIMF, calculate the total SO_2 absorbed up to this time, SADF. This very closely approximates the total sorptive capacity of the sorbent.

$$\text{SADF} = \text{SADE} + \int_{\text{TIML}}^{\text{TIME}} d(\text{TIME}) = \text{SADE} + \int_{0}^{\text{RIL}} \text{TIME}(\text{RI})\, d\,\text{RI} =$$

$$\text{SADE} + \frac{1}{3} A\ \text{RIL}^3 + \frac{1}{2} B\ \text{RIL}^2 + C\ \text{RIL}$$

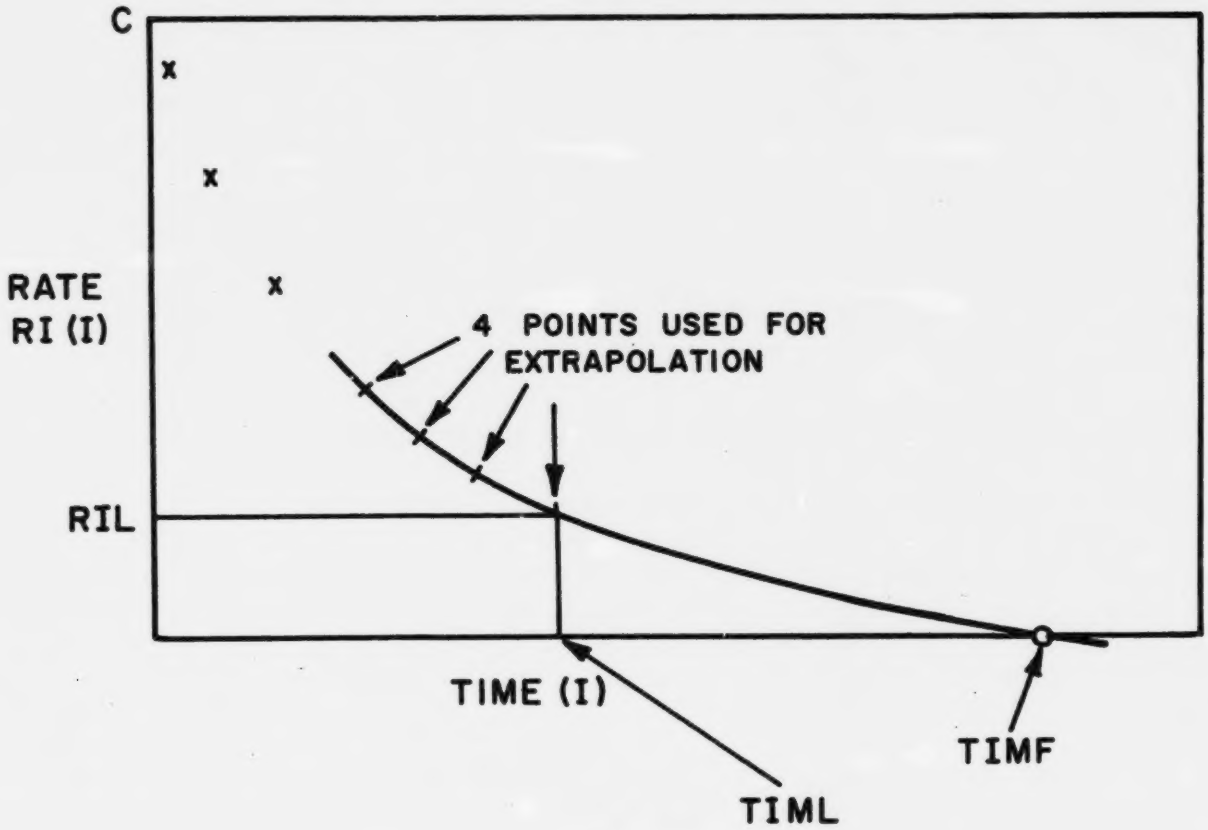


Figure D

Figure C

PLOT OF SORPTION RATE CURVE
RATE(GM SO2/ MIN) VS. LOADING(GM SO2 / GM SOLID)

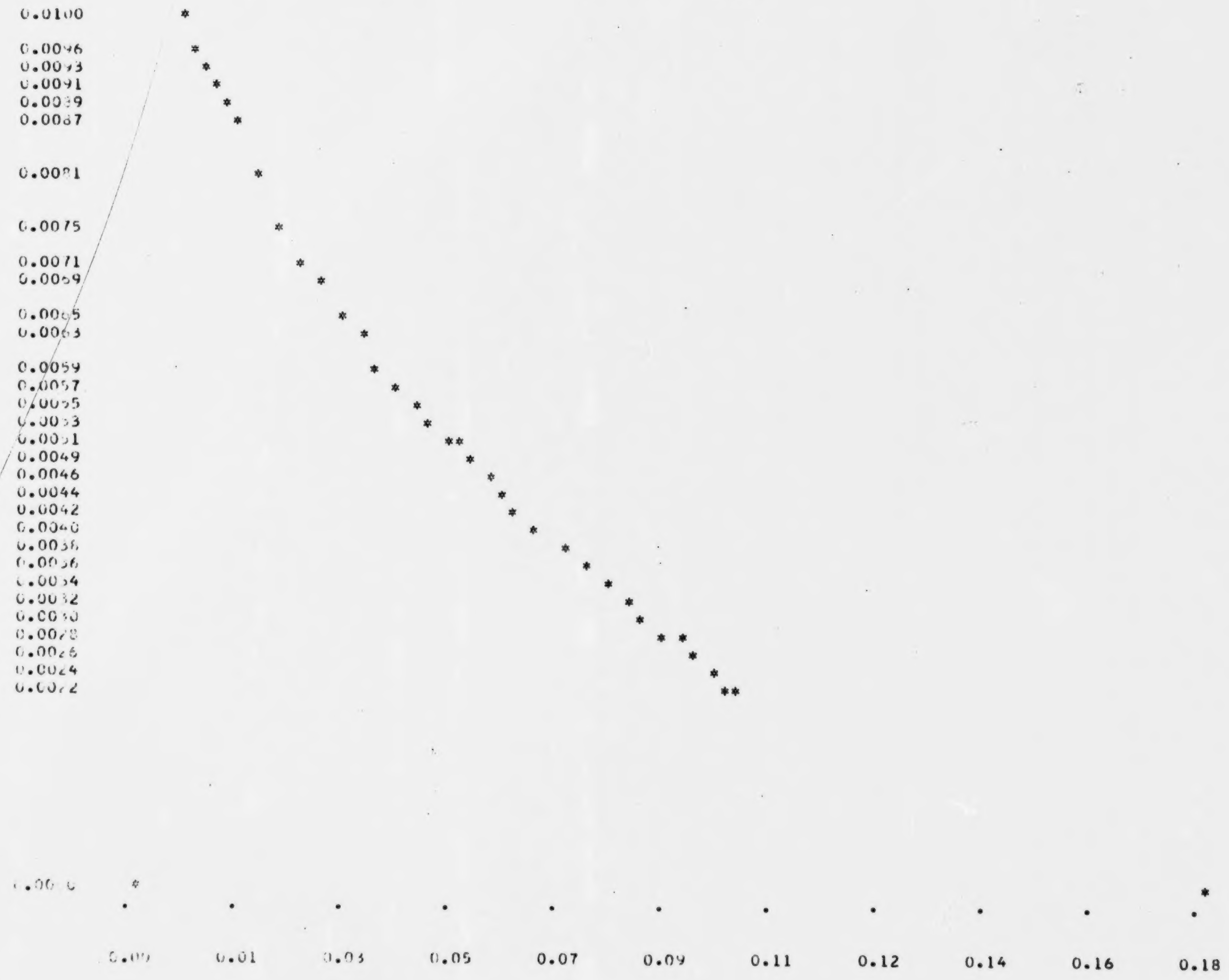


Figure D above shows a computer generated plot of rate vs. sorbent loading for run No. 63. The point in the lower right hand corner is the final sorbent loading, SADF as calculated by the procedure above. Extrapolation of this is an independent way of determining an approximate SADF. In this case, the plot was used as an empirical check on the above calculation of SADF.

OUTPUT

Figure E is a typical computer output showing the results of the calculation for run #63. For each time period TIME(I) recorded in the experiment, the following are listed:

- measured SO_2 effluent concentration, $C_E(I)$, ppm SO_2
- instantaneous sorption rate, RI(I), gm. SO_2/min.
- solids loading, W(I), gm. SO_2/min. sorbent
- fraction of total solids loaded, $\frac{W(I)}{SADF}$

Also included is a listing of the computer program used to perform the calculations described above.

Figure E

```
C       PROGRAM TO DO CALCULATIONS FOR SO2 REMOVAL STUDY
C  G.E. MOEHRINGER
      DIMENSION NA(79)
      DIMENSION RIS(10),TIS(10)
      DIMENSION TBL(75),VBL(75)
      DIMENSION A(150)
      DIMENSION TIME(75),CSE(75)
      DIMENSION CS(75),RI(75),SAD(75),RIA(75)
      DIMENSION SACT(75),SLT(75),RIAD(75)
      DIMENSION TDIVT(75),RRECI(75),S13(75)
      DIMENSION NTITL(6,75)
      DIMENSION ANG(9)
      DATA NINE / '9' /
      DATA NBLAN /' ' /
      NR= 2
      NW = 5
      NP = 2
      READ (NR,996) BLANK,ANG
  996 FORMAT ( 10A1 )
C     READ BLANK DATA
      CF = 3500.0
      CALL DATR( TBL,VBL,TA,X,Y,NTBL,TE,CF,CI,TF )
  699 CONTINUE
      WRITE ( 5,58)
   58 FORMAT ( 1H1 // ' CALCULATIONS FOR SO2 ADSORBENTS' / )
C       READ RUN CONSTANTS
      READ (NR,5) FBLSO,UBLSO,FCONC
      READ ( NR,5) WEI,TEMP,FLOW,NPRB,NBLOT
      READ ( NR,563) RHS,DIAS
  563 FORMAT ( 5F10.2 )
C       IF   NPRB = 0, NO INTERMADIATE PRINTOUT
C       IF NBLOT = 99 , WON'T USE BLANK CORRECTION
    5 FORMAT ( 3F10.2,12X,2I3 )
      WRITE ( NW,101) FBLSO,UBLSO,FCONC,WEI,TEMP,FLOW
   57 FORMAT ( 80A1)
  101 FORMAT ( // F10.2, ' MV AT ZERO SO2 ' /  F10.2 ' MV AT',  F10.2,
     1 ' PPM SO2'/ ' SAMPLE WT , GM. ', F10.2  /
     2 ' TEMPERATURE, DEG. C., ' F10.2  / ' FEED RATE, LITERS/MIN ',
     3 F10.2     )
      NNN = 1
      DO 90 I=1,80
   90 NA(I) = NBLAN
      READ (NR,57) NA
      WRITE ( NW,304) NA
  304 FORMAT (1X,79A1)
      DO 93 I=1,75
      NTITL(1,I) = NA(I)
   93 CONTINUE
      GO TO 62
   60 CONTINUE
      WRITE ( NW,304) NA
      DO 94 I=1,75
      NTITL(NNN,I) = NA(I)
   94 CONTINUE
   62 CONTINUE
      NNN = NNN+ 1
      DO 91 I=1,80
   91 NA(I) = NBLAN
      READ ( NR,57) NA
```

Figure E (Cont'd)

```
      DO 69 I=1,7
      IF( NA(I) -NINE ) 60,69,60
   69 CONTINUE
       NZO = 0
      III = 1
   63 CONTINUE
      READ (NR,70) TIN,XRES,T3
   70 FORMAT (1X,F10.2,5X,F9.2,4X,F10.2)
      IF ( NPRB) 71,72,71
   71 CONTINUE
      WRITE (NW,70) TIN,XRES,T3
   72 CONTINUE
      IF ( TIN - 99999.0) 50,54,54
   54 CONTINUE
      WRITE (NW,55)
   55 FORMAT (' END OF DATA ' )
      WRITE (NW,7) NZO
    7 FORMAT ( 1X,I5 )
      IF ( NPRB) 205,206,205
  205 CONTINUE
      DO 200  I=1,NZO
      T = TIME(I)
      CALL CALCV (TE,TA,CF,TF,CI,X,Y,TBL,VBL,T,V,NTBL )
      DELTA = V - CSE(I)
  200 CONTINUE
  206 CONTINUE
      RIA(1) = 0.0
      SAD(1) = 0.0
C     CALCULATE INSTANTANEOUS ADSORPTION RATE, RI(I)
C     AND SO2 ADSORBED, SAD(I)
C     RI(I) SHOULD BE THE RATE MIDWAY BETWEEN POINT (I) AND  POINT I+1
      DO 300 I=1,NZO
C     GET AUG TIME, TBAR
      TBAR = TIME(I)
C     GET CORRECTION AT TBAR, VOUT
      CALL CALCV (TE,TA,CF,TF,CI,X,Y,TBL,VBL,TBAR,VOUT,NTBL)
      CS(I) = VOUT - CSE(I)
      IF ( CS(I)) 315,316,316
  315 CONTINUE
      WRITE(NW,317) TBAR,CSE(I),VOUT
  317 FORMAT ( / ' BLANK CONCENTRATION LESS THAN RUN CONCENTRATION, DIFF
     1ERENCE SET TO ZERO  ' /
     2 '  TIME = ', F10.2, ' BLANK CON = ', F10.2, ' PPM,  RUN CON = ',
     3 F10.2, ' PPM ' / )
      CS(I) = 0.0
  316 CONTINUE
      IF ( NBLOT - 99) 318,319,318
  319 CONTINUE
      CS(I) = CSE(I)
  318 CONTINUE
C     CORRECTED CONCENTRATION, CS(I)
      RI(I) = ( FLOW/1000.0)* (64.06/22.4 )*( CS(I) /1.0E06)
      IF (I-1) 310,310,311
  311 CONTINUE
      RIA(I) = ( RI(I) + RI(I-1)) / 2.0
      SAD(I) = SAD(I-1) + RIA(I)*(TIME(I) - TIME(I-1))
  310 CONTINUE
  300 CONTINUE
      SADE = SAD(NZO)
```

Figure E (Cont'd)

```
      WRITE (NW,303) SADE
  303 FORMAT ( // ' TOTAL SO2 ADSORBED ', F11.3  )
C     TEST RI(NZO)
      IF(RI(NZO)) 410,410,420
  410 CONTINUE
      SADF = SADE
      SINT = 0.0
      GO TO 500
C  420, FIND TIMF, TIME AT WHICH RI IS ZERO
C     FIT TIME VS. RI USING A QUADRATIC FORM
C     TIME = U + V*RI + W*RI*RI
  420 CONTINUE
  571 CONTINUE
      READ (NR,558) N,M
      IF(N - 99) 570,590,570
  570 CONTINUE
  558 FORMAT ( 2I5)
C     N= NUMBER OF POINTS
C     7 = DEGREE OF EQUATION
      VV = 0.0
      WW = 0.0
      U = 0.0
      V =0.0
      W = 0.0
      I=10
      J=1
  561 CONTINUE
      K= NZO - 10 + J
      RIS(J) = RI(K)
      TIS(J) = TIME(K)
      J= J + 1
      IF(J-10) 561,561,562
  562 CONTINUE
      CALL POLGM(RIS,TIS,U,V,W,WW,VV,10,N,M)
      GO TO ( 501,502,503,504,505) ,M
  501 CONTINUE
      W = 0.0
  502  CONTINUE
      WW = 0.0
  503 CONTINUE
      VV = 0.0
  504 CONTINUE
  505 CONTINUE
      TIMF = U
      RIL = RI(NZO)
C     FIND TOTAL SO2 ADSORBED AT TIMF
C     SINT = SUM(RI(TIME)*D(TIME)) = SUM(TIME(RI)*D(RI))
      SINT = (1.0/3.0)*W*RIL*RIL*RIL + 0.5*V*RIL*RIL +U*RIL
     1 + (1.0/4.0)*WW*RIL*RIL*RIL*RIL
     2  +VV*(1.0/5.0)*RIL*RIL*RIL*RIL*RIL
      SADF = SADE + SINT
  500 CONTINUE
      WRITE(NW,430) TIME(NZO),SADE,TIME(NZO),TIMF,SINT,SADF
  430 FORMAT( //' SO2 ADSORBED,GMS. '/
     1 ' UP TO' , F10.2, '  MIN,', 2X,F10.5 /
     1 ' FROM ', F10.2, ' MIN TO ',F10.2, ' MIN, ' , F15.5 /
     2 ' TOTAL,' , F15.5)
      GO TO 571
  590 CONTINUE
```

Figure E (Cont'd)

```
      MMM = NNN -1
      WRITE (NW,704) ((  NTITL(I,J),J=1,75), I=1,MMM )
  704 FORMAT  (1H1 // 6( 1X,75A1/) /)
      WRITE (NW,702)
  702 FORMAT (      //25X,'CALCULATED RESULTS - SO2 REMOVAL STUDY'  //
     1' TIME         SO2 EXIT            SORPTION           LOADING
     3FRACTION ' /
     2'              CONCENTRATION        RATE
     4 SORBED  '/
     4' MIN.         (PPM SO2)          (GM SO2/MIN)   (GM SO2/GM SOLID)'/)
      DO 700 I=1,NZO
C     CALCULATE LOADING
C     LOADING BASED ON TOTAL SOLIDS, SLT
      SLT(I) =SAD(I) / WEI
C     FRACTION SOLIDS STILL ACTIVE , SACT
       SACT(I) = SAD(I) / SADF
C     INSTANTANEOUS RATE BASED ON ACTIVE SOLIDS, RIAD
      SSS = WEI*(1.0 - SACT(I))
      RIAD(I) = RI(I) / SSS
      WRITE (NW,701) TIME(I),CSE(I),RI(I),SLT(I),SACT(I)
  701 FORMAT(1X,F5.2,4X,F10.2,3X,E15.3,5X,F10.3,7X,F10.3 )
  700 CONTINUE
      ZONE = 1.0
      ZERO = 0.0
      F3500 = 3500.0
      SLF = SADF / WEI
      WRITE (NW,701) TIMF,F3500,ZERO,SLF,ZONE
C     PLOT DATA
      WRITE (NW,697)
  697 FORMAT ( 1H1 / 25X,' SORPTION CURVE ' / 25X,' PLOT OF SO2 EXIT CON
     1CENTRATION VS. TIME '  / )
      NZQ = NZO + 1
      DO 610 I=1,NZQ
      A(I) = CSE(I)
      II = NZQ +  I
      A(II)=  TIME(I)
  610 CONTINUE
      NO= 1
      A(NZQ ) = 3500.0
      II = 2*NZQ
      A(II) = TIMF
      CALL CLOT(NO,A,NZQ,2,50,1,ANG,BLANK)
C     PLOT SORPTION RATE CURVE
      WRITE(NW,804)
  804 FORMAT (1H1/25X,' PLOT OF SORPTION RATE CURVE '  /
     I 25X,' RATE( GM SO2/ MIN ) VS. LOADING( GM SO2 / GM SOLID) ' /)
      NZQ = NZO + 1
      DO 810 I=1,NZQ
      A(I) = RI(I)
      II = NZQ + I
      A(II) = SLT(I)
  810 CONTINUE
      A(NZQ) = 0.0
      II = 2*NZQ
      A(II) = SLF
      NO = 1
      CALL CLOT (NO,A,NZQ,2,50,1,ANG,BLANK )
      WRITE(NW,601)
  601 FORMAT  ( 1H1 / '  TIME      S(FRACTION)     1/RATE    T/TAU    '/)
```

Figure E (Cont'd)

```
      II = 0
      DO 605 I=1,NZO
      TDIVT(I) = TIME(I) / TIMF
      IF (SACT(I)) 710,710,720
  710 CONTINUE
      GO TO 605
  720 CONTINUE
      II = II + 1
      RRECI(II) = 1.0 / RI(I)
      SSS=(1 - SACT(I))**0.33333
      S13(II)  = (1.0 - SSS)  / SSS
      WRITE (NW,602) TIME(I),SACT(I),RRECI(II),TDIVT(I)
  602 FORMAT ( 1X,5F10.3   )
  605 CONTINUE
      WRITE (NW,681)
  681 FORMAT ( 1H1 / 25X, ' PLOT OF SORPTION RATE CURVE ' /
     1 25X,' LOG OF RATE VS. LOG OF LOADING ' / )
      DO 811 I=1,II
      III= II + I
      A(III) = ALOG(1000.0*SLT(I))
      A(I) = ALOG(1000.0*RI(I))
  811 CONTINUE
      CALL CLOT(NO,A,II,2,50,1,ANG,BLANK)
C     FIT  1/R VS. S13
C     1/R = U + V*S13
      N=II
      M= 1
      VV= 0.0
      WW= 0.0
      U = 0.0
      V = 0.0
      W = 0.0
       CALL POLGM(S13,RRECI,U,V,W,WW,VV,N  ,N,M)
      SLOPE= V
      FINT = U
      WRITE (NW,622) SLOPE, FINT
  622 FORMAT  ( '  SLOPE =', F10.3 / '  INTERCEPT =', F10.3 / )
      TTTF = ( 9.0/5.0 ) * TEMP + 32.0
      VRAT = 359.0 *( TTTF +460.0 )/ 520.0
      CO = FCONC / ( 1.0E06 * VRAT )
      FKC = ( RHS*DIAS*SADF) /(192.0*CO *FINT )
      DIFF = DIAS*FKC *FINT / SLOPE
      WRITE(NW,564) FKC,DIFF
  564 FORMAT ( // ' MASS TRANSFER COEFFICIENT KSUBC ' , E15.3, ' FT/HR'/
     1 ' EFFECTIVE DIFFUSIVITY ',E15.3, ' SQFT/HR'  )
C     PLOT  1/R  VS  S13
      WRITE  (NW,621)
  621 FORMAT ( 1H1/  25X,' RECIPROCAL RATE PLOT' / 25X,' RECIPROCAL RATE
     1 VS. ( 1-(1-S)**1/3 ) / (1-S)**1/3 ' /)
      II = II + 1
      DO 650 I=1,II
      A(I) = RRECI(I)
      III = I+ II
      A(III) = S13(I)
  650 CONTINUE
      A(II) = U
      III = 2*II
      A(III) = 0.0
      CALL CLOT(NO,A,II,2,50,1,ANG,BLANK)
```

Figure E (Cont'd)

```
C     CHECK AGREEMENT ON TIME
      WRITE (NW,623) (( NTITL(J,I),I=1,50), J=1,MMM )
  623 FORMAT  ( 1H1 / ' COMPARISION OF DATA WITH AVCO MODEL ' /
     16(1X,50A1/) / )
      WRITE (NW,624)
  624 FORMAT ( ' TIME-DATA    TIME-CALC.   DELTA          DELTA**2  ' /)
      SQTER= 0.0
      STER = 0.0
      SQTRR= 0.0
      DO 630 I=1,NZO
      SSS = SACT(I)
      SSSS = (1.0 - (( 1.0 - SSS)**0.66667)) *(3.0/2.0 )
      TCL = SLOPE * SSSS - ( SLOPE - FINT ) * SSS
      DEL = TIME(I) - TCL
      STER = STER + ABS(DEL/TIME(I))
      DELSQ =  DEL**2
      SQTER= SQTER + DELSQ
      SQTRR = SQTRR + DELSQ / TIME(I)
      SQTER = SQTER + DELSQ
      WRITE (NW,625) TIME(I),TCL,DEL,DELSQ
  625 FORMAT ( 1X,6F10.2 )
  630 CONTINUE
      AVSQE = SQTER / NZO
      AVSQQ = SQTRR * 100.0
      AVGER = STER / NZO  *100.0
      WRITE ( NW,626) AVGER,AVSQE,AVSQQ
  626 FORMAT ( /  ' AVERAGE ERROR,PCT = ', F15.3  /
     1 ' AVERAGE RMS ERROR=', F15.3  /  ' RMS PCT=', F15.3    )
C     PLOT   T/TAU  VS.  CONVERSION
      WRITE  (NW,851)
  851 FORMAT ( 1H1/  25X,' PLOT OF EXTENT OF SORPTION VS. FRACTIONAL TIM
     1E FOR COMPLETE SORPTION ' /  )
      NZQ = NZO + 1
      DO 860 I=1,NZQ
      A(I) = SACT(I)
      II = NZQ + I
      A(II)= TIME(I) / TIMF
  860 CONTINUE
      A(NZQ) = 1.0
      II = 2*NZQ
      A(II) = 1.0
      NO = 1
      CALL CLOT(NO,A,NZQ,2,50,1,ANG,BLANK )
C     FIT   T/TAU  VS. CONVERSION
      WRITE (NW,661)
  661 FORMAT ( 1H1 / ' COMPARISIONS OF VARIOUS KINETIC MECHANISMS ' /
     1'  OBSERVED          GAS DIFFUSION LIMITING       SOLID DIFFUSION LIM
     2ITING               CHEMICAL REACTION LIMITING '  /
     3'  T/TAU            T/TAU CALC     DELTA              T/TAU  CALC
     4DELTA              T/TAU CALC      DELTA ' /  )
      PDTG = 0.0
      PDTD = 0.0
      PDTR = 0.0
      DO 670 I=1,NZO
      SSS= 1-SACT(I)
      TDTG =  SACT(I)
      TDTGD = TDIVT(I) - TDTG
      PDTG = PDTG + ABS(TDTGD/TDIVT(I))
      TDTD = 1.0 - 3.0*(SSS**0.66667) + 2.0*SSS
```

Figure E (Cont'd)

```
      TDTDD = TDIVT(I) - TDTD
      PDTD = PDTD + ABS(TDTDD/TDIVT(I))
      TDTR = 1.0 - SSS**0.33333
      TDTRD = TDIVT(I) - TDTR
      PDTR = PDTR + ABS(TDTRD/TDIVT(I))
      WRITE (NW,662) TDIVT(I),TDTG,TDTGD,TDTD,TDTDD,TDTR,TDTRD
  670 CONTINUE
  662 FORMAT (1X,F7.3,6F15.3 )
      PCTG = PDTG / NZO  *100.0
      PCTD = PDTD / NZO  *100.0
      PCTR = PDTR / NZO  *100.0
      WRITE (NW,663) PCTG,PCTD,PCTR
  663 FORMAT ( ' AVERAGE PERCENT ERROR, COMPARED TO KINETIC MODELS ' /
     1 ' GAS FILM LIMITING ',F15.1 / ' DIFFUSION LIMITING ' ,F15.1 /
     2 ' REACTION LIMITING ' , F15.1 )
      GO TO 699
  698 CONTINUE
      CALL EXIT
   50 CONTINUE
      NZO = NZO + 1
      TIME(NZO) = TIN
      CSE(NZO) = T3
      GO TO 63
      END
```

APPENDIX II

CARBON-SULFUR DIOXIDE SORPTION STUDIES

OFFICE MEMORANDUM
FMC CORPORATION
CENTRAL RESEARCH DEPARTMENT
PRINCETON, N. J. 08540

COPY TO A. J. Durbetaki
A. V. Hanley
S. P. Marcus
J. C. Wasilewski

DATE February 6, 1970

TO L. D. Friedman

FROM L. R. Beck

SUBJECT CARBON-SULFUR DIOXIDE SORPTION STUDIES

The Cahn recording electrobalance, employed as a thermo-analytical tool, was used to study the adsorption - desorption of SO_2 on carbon and to measure the effects on the carbon sorbent. In this system, a 20-40 mesh cut of Nuchar carbon was placed in a quartz cup suspended from the electrobalance in a combustion tube. The apparatus is designed for the introduction of SO_2, other gases and moisture at set flow rates. The unit could be operated at ambient temperature, isothermally at elevated temperatures or programmed at several rates to elevated temperatures. In this work, adsorptions were carried out at ambient temperature and the desorptions were measured during a programmed temperature increase from ambient to 350°C. The system was operated with SO_2, moist and dry helium, air, nitrogen, and hydrogen passing over the carbon samples during different phases of the study.

Summary

Data from the study showed that carbon was more reactive in moist helium than in dry helium. The presence of air and moisture in the sorptive step had the most pronounced effect on the amount of SO_x absorbed and subsequently driven off at 170-350°C. In the desorption cycle, hydrogen did not lower the temperature required for desorption of sorbed SO_x material.

Experimental

Prior to starting the sorption experiments, the Nuchar carbon sample was held at 350°C for several hours to drive all volatiles from the carbon. After this conditioning, the carbon weighed 12.4 mg. Helium was passed over the sample during the pretreatment and during all other experiments. Other gases were introduced during various stages of experimentation. The helium was moistened by bubbling it through a column of water. The vapor pressure of water in the helium stream was approximately 25 mm. In one set of tests, dry helium was used in order to note any differences which resulted from the presence or absence of water in the sorption system.

A series of test runs were made to establish basic conditions for carrying out the study. In moist helium the carbon sorbed 15 weight percent water in one hour, and approximately 30 weight percent in 18 hours. To maintain uniform conditions from run to run and to be able to make runs in a reasonable time, moist helium was passed over the carbon until it sorbed 15 weight percent moisture before starting a run.

Earlier work in a dry helium system had shown that SO_2 sorption began to level out after a half-hour treatment with helium containing SO_2. Therefore, all SO_2 sorptions were made for the half hour. The SO_2 was introduced at 9.2 ml/min. as a 1% mixture with dry helium in combination with moist helium plus air, hydrogen or nitrogen. When 1% SO_2 in dry helium was added in combination with nitrogen or more helium, a 6.4 weight percent adsorption was measured in one half hour. The rate of SO_2 adsorbed could not be measured when it was added in combination with moist helium, because the carbon lost some moisture during the SO_2 sorption and because the addition of the SO_2-helium gas mixture to the moist helium stream caused a change in moisture content of the total gas stream.

TABLE I

Gas Flow

Gas	Flow Rate
Air	5.0 ml./min.
Hydrogen	9.4 ml./min.
Nitrogen	10.0 ml./min.
SO_2-1% in helium	9.2 ml./min.
Moist or dry helium	12.2 ml./min.

Water and SO_2 sorptions were carried out at room temperature. During desorption, the sample was heated at a rate of 6°C/min. from room temperature to 350°C, and the sample was held at 350°C until the weight loss showed no change over a 10 minute period. The major portion of the sorbed water and SO_2 was desorbed at or below 100°C. Tests showed that carbon treated with SO_2 retained a volatile material which was not driven off, however, until higher temperatures. Tests also showed that in the absence of SO_2 virtually all water was desorbed below 170°C, and that virtually no SO_2 was removed below this temperature. Therefore, the effects of different gases used in the sorption-desorption process study were compared by measuring the amount of material that was desorbed while heating the carbon from 170 to 350°C. The upper temperature limit was chosen since it was high enough to drive off the SO_x compound but did not decompose the Nuchar carbon appreciably. Material desorbed between 170 and 350°C probably is SO_3, as sulfuric acid, or chemisorbed sulfur dioxide. These experiments measured changes in weight of the sorbent and the temperature at which they occurred. However, no means were provided for identifying the material desorbed from the carbon.

Table II shows the carbon weight losses obtained when the sorption-desorption cycles were made with mixtures of dry nitrogen and both moist and dry helium. With dry nitrogen and helium, a small loss in weight equivalent to 0.1% of the 12.4 mg carbon sample was observed between 170 and 350°C. In runs with the dry gases, no additional weight loss was observed when the carbon was held at 350°C for an additional 30 minutes. The small loss in weight observed in this run might be partially attributed to the buoyancy effects of the gases passing around the sample. For this reason, flow rates of gases were maintained as similar as possible throughout all experiments. Cycling the dry nitrogen and helium through the sorption-desorption cycle caused a carbon weight loss of 0.004 mg or only 0.03 weight percent of the carbon. This 0.03% loss represents the minimum detectable change which could be measured in these experiments.

When moist helium was used throughout the cycle in a similar experiment, as shown in Table II, most of the moisture desorbed at 100°C but the sample showed a 0.4 weight percent loss between 170 and 350°C. At 350°C the rate of weight loss slowed but did not level out completely as was the case when the dry gases were employed. The carbon weight loss from cycle to cycle was increased to 0.1%, as compared with the 0.03% observed with the dry gases. These data show that moisture actively affects the carbon. This may be due to steam attacking active sights on the carbon to produce carbon dioxide as in the classical water gas reaction, but the relatively low temperatures permit only a minor attack on the carbon by the moisture.

TABLE II

% Loss of Carbon in Helium Gas[1]

	Moist Helium & Dry Nitrogen	Dry Helium & Dry Nitrogen
Typical losses from 170-350°C	0.4%	0.1%
Typical loss of carbon from cycle to cycle	0.1%	.03%

[1] Original conditional weight of carbon 12.4 mg.

A series of experiments was made in which a mixture of SO_2, moisture and helium was passed over the carbon during the sorption stage and either nitrogen or hydrogen was added to the moist helium in the desorption stage. In some runs, air or nitrogen was also added during the sorption operation. The experimental data for these runs are summarized in Table III in the order in which they were carried out and are listed in Table IV according to the gases used during the sorption-desorption processes. These data show variations in the weight losses which may be attributed to changes in the sorptive capacity of the carbon over this time.

The average weight loss between 170 and 350°C for several experiments when nitrogen was used in the desorptive cycle is 2.1%. The average value for two experiments using hydrogen during desorption is 1.9%. This represents no significant difference, indicating that the reductive properties of hydrogen do not improve the total desorption of the more highly bound material from the carbon under the experimental conditions employed. The desorptive properties of these two gases were compared more critically by measuring the weight losses over several temperature increments between 172°-343°C. These data are found on Table VI. Contrary to what may be expected there is a greater desorption at the lower temperatures when using nitrogen than when hydrogen is in the desorbing gas. Nitrogen was added to the gas stream in the sorption step of one experiment (#5) with hydrogen. This had no significant effect on the results.

When air was introduced during the sorption of SO_2 (Experiments 3, 6, 8, 13, 14, 15 and 16) a significant increase in the amount of material held on the carbon at elevated temperatures was noted. The weight loss from 170°-350°C, using nitrogen in the desorption stage was increased to 3.0% (Experiments 3, 6 and 8). Using hydrogen in the desorption the value averaged 3.2% (Experiments 13, 14, 15 and 16). The average of 3.1% for all experiments was well above the 2.0% average for those experiments in which no air was introduced. These data showed that the air caused oxidation of sulfur dioxide to the trioxide which is retained more strongly by the carbon sorbent.

The carbon loss for a complete sorption-desorption cycle for all experiments in Table III averaged 0.08 weight percent. This figure did not vary significantly with the gases used during the sorptions or desorptions (see Table IV), and this 0.08% value is similar to the 0.10% carbon loss found in moist helium alone.

SO_2 sorption experiments using dry helium in both the sorption and desorption cycles are listed in Table V. The weight increase due to sorption of SO_2 averaged 6.4% but the values varied between 5.8-6.6%, showing measurable variations even though conditions were kept the same. As expected, substituting nitrogen for air during sorption decreased the amount of volatile material retained on the carbon. A comparison of the carbon lost on cycling in this dry system vs. the moist helium (compare Tables III and V) shows an average loss of 0.05% for the dry system and 0.08% for the moist.

If there are any questions regarding this work or if we can be of further assistance to you do not hesitate to contact us.

L. R. Beck
L. R. Beck

LRB/kr

TABLE III

% LOSS - MOIST HELIUM

Experiment	Gases Flowing Past Sample[1]		% Loss	% Loss
No.	Sorbing	Desorbing	170-350°C	on Cycling
1	SO_2 H_2O He	H_2O He N_2	2.2	.13
2	SO_2 H_2O He	H_2O He H_2	2.0	.03
3	SO_2 H_2O He air	H_2O He N_2	3.1	.13
4	SO_2 H_2O He	H_2O He N_2	1.8	.06
5	SO_2 H_2O He N_2	H_2O He H_2	1.8	.10
6	SO_2 H_2O He air	H_2O He N_2	3.1	.06
7	SO_2 H_2O He	H_2O He N_2	1.7	.03
8	SO_2 H_2O He air	H_2O He N_2	2.9	.03
9	SO_2 H_2O He	H_2O He N_2	2.6	.10
10	SO_2 H_2O He	H_2O He N_2	2.0	.10
11	SO_2 H_2O He	H_2O He N_2	2.0	.06
12	SO_2 H_2O He	H_2O He N_2	2.1	.06
13	SO_2 H_2O He air	H_2O He H_2	3.4	.10
14	SO_2 H_2O He air	H_2O He H_2	3.1	.10
15	SO_2 H_2O He air	H_2O He H_2	3.3	.13
16	SO_2 H_2O He air	H_2O He H_2	3.0	.06
				Av. = .08

[1] For rate of flow see Table I

TABLE IV

Summary from Table III

% Loss - Moist Helium

Experiment No.	Gases Flowing Past Sample		Average % Loss 170-350°C	Average % Loss on Cycling
	Sorbing	Desorbing		
1, 4, 7, 9, 10, 11, 12	SO_2 H_2O He	H_2O He N_2	2.1	.08
2, 5*	SO_2 H_2O He	H_2O He H_2	1.9	.07
3, 6, 8	SO_2 H_2O He air	H_2O He N_2	3.0	.07
13, 14, 15, 16	SO_2 H_2O He air	H_2O He H_2	3.2	.10

* Nitrogen also used in sorption step of this experiment

TABLE V

% Loss - Dry Helium

Experiment No.	Gases Flowing Past Sample		% Gain SO_2 Sorption	% Loss 170-350°C	% Loss on Cycling
	Sorbing	Desorbing			
17	SO_2 He air	He N_2	6.6	0.7	.06
18	SO_2 He air	He N_2	6.5	0.8	.06
19	SO_2 He N_2	He N_2	5.8	0.5	.06
20	SO_2 He N_2	He N_2	6.6	0.6	.06
21	SO_2 He N_2	He N_2	6.3	0.5	.03
		Av. =	6.4	Av. =	.05

TABLE VI

Comparison of Desorption with Nitrogen or Hydrogen

	% Lost			
	Desorbing Gas Nitrogen		Desorbing Gas Hydrogen	
Temperature Increment (°C)	Experiment # 6	Experiment # 8	Experiment # 14	Experiment # 16
172-197	8.1	7.0	2.7	2.9
197-222	8.1	12.7	4.0	2.9
222-246	10.8	9.9	6.7	8.7
246-272	13.5	11.3	13.3	10.1
272-295	13.5	11.3	16.0	17.4
295-319	24.3	22.5	29.3	29.0
319-343	21.6	25.4	28.0	29.0
	99.9	100.1	100.0	100.0

APPENDIX III

REGENERATION OF SODIUM CARBONATE

REGENERATION OF SODIUM CARBONATE

A brief study was made of the Na_2CO_3 regeneration reactions described on pages 103 and 106 above. This study had to be terminated by expiration of the contract before optimum reaction conditions could be obtained. Therefore, these results merely indicate trends.

OPERATING PROCEDURE

The sodium salt, calcium carbonate and coal or active carbon was placed in a platinum or nickel crucible and heated in a tube furnace to the indicated temperatures. A slow stream of nitrogen was bled through the furnace throughout the run to remove any sulfur dioxide that might be evolved during the heating period. The time of the experiment was the time at which the reactants were at the indicated temperature.

To analyze the products, the crucibles were removed from the furnace, and cooled in a desiccator. The melts were extracted with water and the insolubles were filtered, dried, and analyzed for calcium sulfide and calcium carbonate. The filtrate was analyzed for sodium carbonate and sodium sulfide. The sodium salts dissolved readily, the calcium salts only slightly. (Some hydrolysis of CaS occurred.) With aqueous solutions of pure compounds, recoveries of sodium carbonate, sodium sulfide, sodium sulfate and sodium sulfite from mixtures with calcium sulfide and calcium carbonate were in excess of 95 weight percent.

Carbonate was measured by determining the amount of CO_2 evolved in acidification. The evolved CO_2 was collected in a known excess of barium hydroxide solution. The unreacted barium hydroxide was determined by acid titration and the amount of evolved CO_2 found by difference. Sulfur was determined by acidifying an aliquot of the filtrate or an aqueous suspension of the solids and passing a stream of nitrogen through the heated solution until all H_2S was evolved. The hydrogen sulfide was titrated with iodine solution.

EXPERIMENTAL RESULTS

Data for several runs made with this system are shown in Table III-1.

TABLE III-1

Formation of Na_2CO_3 From Na_2SO_3 and Na_2SO_4

Run No.		Temp, °C	Time Hr	% Na_2CO_3 Recovered	% Na_2S	% CaS	% $CaCO_3$
1	1g Na_2SO_3, 1g $CaCO_3$, 0.5g Coal	1000	1	11.1	-	15	-
3	1g Na_2SO_3, 1g $CaCO_3$, 0.5g Coal	1000	2	17.0	35.2	16.4	5.5
5	1g Na_2SO_3, 1g $CaCO_3$, 0.5g Coal	1100	1	12.2	26.5	29.4	5.9
2A	2g Na_2SO_3, 2g $CaCO_3$, 1g carbon	1100-1200	5	11.5	-	23.1	1.5
6	1g Na_2SO_4, 1g $CaCO_3$, 0.5g Coal	1100	1	11.2	40.2	21.9	7.1
2	1g $Na_2S \cdot 9H_2O$, 1g $CaCO_3$, 0.5g Coal	1000	1	31.4	-	31.6	5.5
4	1g $Na_2S \cdot 9H_2O$, 1g $CaCO_3$, 0.5g Coal	1000	2	34.5	-	26.9	9.6
7	4g Na_2SO_4, 1.4g Coal	1000	1	-	48.0	-	-
8	4g Na_2SO_3, 1.2g Coal	1000	1	-	42.8	-	-

When both sodium sulfite and sodium sulfate were reacted with coal and calcium carbonate, the amount of sodium carbonate recovered varied between 11 and 17% of theory. The reaction was relatively insensitive to temperatures between 1000 to 1200°C and to residence times of from 1 to 5 hours. From 25 to 40 weight percent of the sodium charged was recovered as sodium sulfide. Yields with calcium sulfide varied from 15 to 29%, with somewhat higher yields being obtained at the higher temperatures. From 1 to 7% of the calcium was recovered as calcium carbonate.

This reaction has several drawbacks. The reaction of sodium sulfide with calcium carbonate can take place only after the sodium sulfate or sodium sulfite has been reduced to the sulfide. However, calcium carbonate decomposes to calcium oxide and CO_2 at the temperature at which the reduction of sodium sulfate with coal occurs. Moreover, the decomposition of $CaCO_3$ proceeds faster than the reduction reaction. Thus, little $CaCO_3$ was available to react with Na_2S.

In discussing the LeBlanc Process in which Na_2SO_4 reacted with $CaCO_3$ to form Na_2CO_3, Mellor[77] noted that "the reaction was quite complicated. The reactants were mixed in a bed several inches deep and the upper part was reduced first. The quicklime which had formed in the pasty layer at the surface was converted into calcium carbonate by the CO_2 which formed from reduction of the sodium sulfate in the lower levels and which rose to the top of the bed. As the sodium sulfide fused, it penetrated the $CaCO_3$ and mutual decomposition occurred". This implies that some decomposition of calcium carbonate with elimination of CO_2 occurred rapidly but that in a thick bed there was a continuous recarbonation of the calcium oxide. This regenerated calcium carbonate was then available to react when the sodium sulfide fused. In the shallow crucibles used in this study, the bed of reactants was less than 5 mm deep and the CO_2 probably was evolved from the calcium carbonate long before the sulfite or sulfate was reduced to the sulfide by the carbon. Hence, the large proportion of Na_2S unconverted to the carbonate.

About half the sodium sulfate or sodium sulfite charged in runs 3 and 6 was recovered as sodium sulfide and sodium carbonate. The balance was presumed to be unreduced sodium sulfate, which indicated that two hours is not sufficient time to reduce more than half the sodium sulfate in the static beds used in these studies.

In runs 7 and 8, sodium sulfate and sodium sulfite were reacted with coal in the absence of calcium carbonate, and a similar conversion (48 and 43%, respectively) to sodium sulfide was obtained, which lends support to this slow reduction theory. At this same conversion rate, either Na_2SO_4 or Na_2SO_3 should be converted to Na_2S in over 90% yield in about 4 hours.

In runs 2 and 4, sodium sulfide and calcium carbonate were reacted with coal at 1000°C. The sodium carbonate recovery was over 30%, which is two to three times the carbonate yield obtained when Na_2SO_3 or Na_2SO_4 was reacted similarly. This higher Na_2CO_3 yield probably resulted because the molten sodium sulfide could react with the calcium carbonate before the latter was decarbonated. The longer reaction time in run 4 did not give higher Na_2CO_3 yields presumably because the $CaCO_3$ was entirely converted to CaO in less than one hour.

These results indicate that the reduction of sodium sulfate and sulfite with carbon was relatively slow. In the evaluations shown above, the amount of sodium carbonate needed per hour to treat the flue gas is 205,000 pounds. To regenerate 200,000 pounds of sodium carbonate in an hour, it is necessary to have a regeneration reaction which is relatively rapid. Because carbonation with calcium carbonate is relatively slow, the sizing of reaction kilns raises serious difficulties. Thus, the kinetics of these reactions would appear to rule out their application as originally visualized.

The problem of the metals of construction would also mitigate against the use of this reaction. The FMC Corporation reduces sodium sulfate with carbon to sodium sulfide in an overseas plant that is plagued with serious corrosion difficulties. The brick lining of the furnace requires extensive repairs and replacements. This too would not be suitable for a regeneration type plant handling an excess of 200,000 pounds of sodium carbonate an hour.

TWO-STAGE SODIUM CARBONATE REGENERATION

Another approach to forming Na_2CO_3 from Na_2SO_3 and/or Na_2SO_4 consists of first reducing the sodium sulfite or sulfate to sodium sulfide, and reacting the sulfide with CO_2 in water to form Na_2CO_3 and H_2S. The literature indicated that Na_2SO_3 could be reduced to Na_2S in high yields in short reaction times (page 107 above), and this was confirmed somewhat by the results in Table III-1.

Sodium sulfide can be converted readily to sodium carbonate by bubbling CO_2 through a sodium sulfide solution. Thus, a saturated sodium sulfide solution was carbonated at room temperature and at 90°C until no free liquid was visible. The sodium carbonate was then filtered from the mother liquid by suction and the filtrate was evaporated to dryness. The recoveries and x-ray analyses of the precipitated sodium carbonates and of the dried residue recovered on evaporation of filtrate are shown in Table III-2.

Run 1 was conducted for one hour while a rapid stream of CO_2 was bubbled through the sodium sulfide solution, whereas a slow stream of CO_2 was used in run 2. Solids recoveries were in excess of 100% when the filtrate was evaporated to dryness and the weight of sodium salts in the filtrate was added to the weight recovered by filtration. These high yields are due to water of crystallization. The x-ray patterns showed sodium sulfide containing 5 mols of water of crystallization, the sodium sesquicarbonate, as well as some sodium carbonate with water of crystallization. To determine the hydrate forms, the filtered solids were not dried in an oven before being analyzed by the x-ray but were dried by being pressed between filter papers until no further weight loss on drying was observed.

The data in Table III-2 showed that the precipitated solids contained negligible amounts of sodium sulfide. This was expected from the solubility data, since sodium sulfide is much more soluble than either sodium carbonate, sodium bicarbonate or sodium sesquicarbonate.

The solids filtered in runs 1 and 3 were primarily sodium sesquicarbonate, with only minor amounts of sodium carbonate and sodium bicarbonate. By contrast, the solids

TABLE III-2

Carbonation of Sodium Sulfide Solution

RUN NO.	I	II	III
Charge, g Na_2S	3.25	3.25	3.25
Carbonation Temp, °C	25	25	90
Carbonation Time, Hrs	1	1	1/4
Solids Recovery, %			
Filtered Solids	46	63.8	71.5
Evaporation of Filtrate	-	67.6	64.5
% Na_2S in Solids			
Filtered Solids	0.4	1.9	0.4
Evaporated	-	8.6	11.9
Crystal Structures in Filtered Solids			
Major	Sodium Sesqui-carbonate	$NaHCO_3$	Sodium Sesqui-carbonate
Minor	$NaHCO_3$, Na_2CO_3	Sodium Sesqui-carbonate	$NaHCO_3$ Na_2CO_3

obtained in run 2 were primarily sodium bicarbonate with a small amount of sodium sesquicarbonate. The solids obtained when all filtrates were evaporated to dryness were primarily sodium carbonate and sodium sulfide with traces of sodium bicarbonate or sodium sesquicarbonate.

Kubelka and Jojnos[78] present a somewhat complicated version of the carbonation of sodium sulfide and sodium carbonate solutions by gaseous CO_2. They visualize the formation of sodium hydrosulfide NaHS and the hydrolysis of the NaHS with water according to the equation

$$NaHS + H_2O \rightarrow NaOH + H_2S$$

They state that this reaction proceeds by hydrogen sulfide desorption and that the governing factor of the speed of carbonation is the speed of H_2S desorption from solution. At high temperatures, the $S^=$ ion elimination is greatly increased. The effect of CO_2 concentration on sulfide ion elimination is negligible. However, the composition of a final carbonation solution (i.e. the carbonate or bicarbonate form) is directly dependent on the CO_2 concentration, on the temperature of the solution and, to a lesser degree, on the concentration of the solution.

In the carbonation of sodium sulfide solution, a temperature of 90°C gave an extremely rapid carbonation reaction. The recovery of sodium sesquicarbonate or sodium bicarbonate as major products will actually enhance the attractiveness of a sodium carbonate system since the data presented above showed that sodium bicarbonate and sodium sesquicarbonate sorbed more SO_2 than Na_2CO_3 itself. The recovery of the bicarbonate and sesquicarbonate along with the carbonate would probably give more than the 20 weight percent sorption used in the economic evaluation and would permit some reduction in equipment costs.

APPENDIX IV

COST ESTIMATES FOR SO_2 REMOVAL FROM FLUE GAS WITH SODIUM SESQUICARBONATE AND REGENERATION OF SORBENT BY REDUCTION WITH CARBON

TABLE IV-1

Cost Estimates for SO_2 Removal from Flue Gas With Na Sesquicarbonate and Regeneration of Sorbent by Reduction with Carbon

	H.P.	Quantity	Cost	Labor
Sorber 24 cells 16x16x40			$1,440,000	
Filter Bags 364,000 ft^2 + Accessories			470,000	
Ducts			369,360	
Induced Draft Fans 650,000 acfm		3	149,000	
Drivers (3-850 HP)	2600	3	150,000	
Sorbent Feed System	20		40,000	
Deflation Blower 40,000 cfm			17,700	
Driver	60		2,700	
Spent Sorbent Bin 105T			20,000	
Cyclone			5,200	
Dust Collector Bin + Cyclone			14,400	
Blower & Motor 10,000 cfm	20		3,960	
Bucket Elevator 150T/hr	20		8,720	
Storage Bins 250T ea.		6	240,000	
Conveyor 100 Ft	20		10,980	
	2740		2,941,920	588,400
Belt Feeder, Sorbent 150' x 30"	30		14,720	

TABLE IV-1 (Cont'd)

	H.P.	Quantity	Cost	Labor
Belt Feeder, Coal 50'x18"	10		$ 6,440	
Solids Blender	50		32,400	
Screw Feeder	10		7,640	
Rotary Kiln 16' dia. x 600'		2,550	2,550,000	
Brick Lining			640,000	
Driver	200		3,900	
Calcined Product Conveyor 3' x 75' SS	10		25,240	
Dissolving Tanks 50,000 gal. ea. SS		2	91,000	
Mixer 20 HP ea.	40	2	14,600	
Slurry Pump 1000 gpm	30		6,770	
Ash Filters 600 ft^2 Drum		2	390,000	
Ash Conveyor 50' x 18"	10		6,440	
Filtrate Pump	30		6,770	
	420		3,795,920	379,600
Clarified Liquor Tank, 50,000 gal. SS			45,500	
Liquor Pump 1000 gpm 50 HP	100	2	9,800	
Carbonation Tower 42' dia. x 30' Pack			127,500	
Ducts from Calciner			23,600	
Tower Draft Blower 108,000 acfm			89,000	
Driver	720		41,500	

TABLE IV-1 (Cont'd)

	H.P.	Quantity	Cost	Labor
Slurry Thickener 60	10		64,600	
Overflow Pump 1000 gpm	50		9,800	
Evaporator-Crystallizer	1500		1,170,000	
Slurry Pump	20		6,770	
Filtrate Return Pump	20		6,770	
Centrifuge Cont. Screen 36 in. 75 hp	225	3	720,000	
Conveyor 50 ft	20		9,830	
Screw Feeder	10		7,640	
Spray Dryer 30 ft			477,000	
Elevator to Storage 150 T/hr	20		8,720	
	2695		2,818,030	282,000
Insulation			200/ft^2	100/ft^2
Flue Gas Sorber 48,000 ft^2			96,000	48,000
Flue Gas Ducts 10,000 ft^2			20,000	10,000
Vessel, Carbonator 6400 ft^2			12,800	6,400
Gas Ducts 3400 ft^2			6,800	3,400
Evaporator 17,800 ft^2			35,600	17,800
Liquor Tanks 5000 ft^2			10,000	5,000
Thickener 1900			3,800	1,900
Piping 10,000			20,000	10,000
			205,000	102,500

TABLE IV-1 (Cont'd)

	Cost	Labor
Credit for Elimination of Electrical Precipitator		
Electrical Precipitator Cost, for 1.88 x 10^6 cfm, installed	$3,200,000	
Operating Credit - [72]		
Capital (0.14) (3,200.000)	610,000	
Maintenance (0.05) (3,200,000)		
Power 0.5 kw/1000 cfm	41,200	
Total Credit	$ 651,200	

APPENDIX V

APPARATUS AND OPERATING PROCEDURE FOR THE DETERMINATION OF THE FORMS OF SULFUR IN REGENERATION GASES

APPARATUS AND OPERATING PROCEDURE FOR THE DETERMINATION OF THE FORMS OF SULFUR IN REGENERATION GASES

A technique was established to determine the forms in which sulfur was present in the gases used to regenerate copper-impregnated silica-alumina sorbents. The apparatus, patterned after that suggested by Flint [J. Soc. Chem., Ind., 67, 2 (1948)], is shown in Figure V-1.

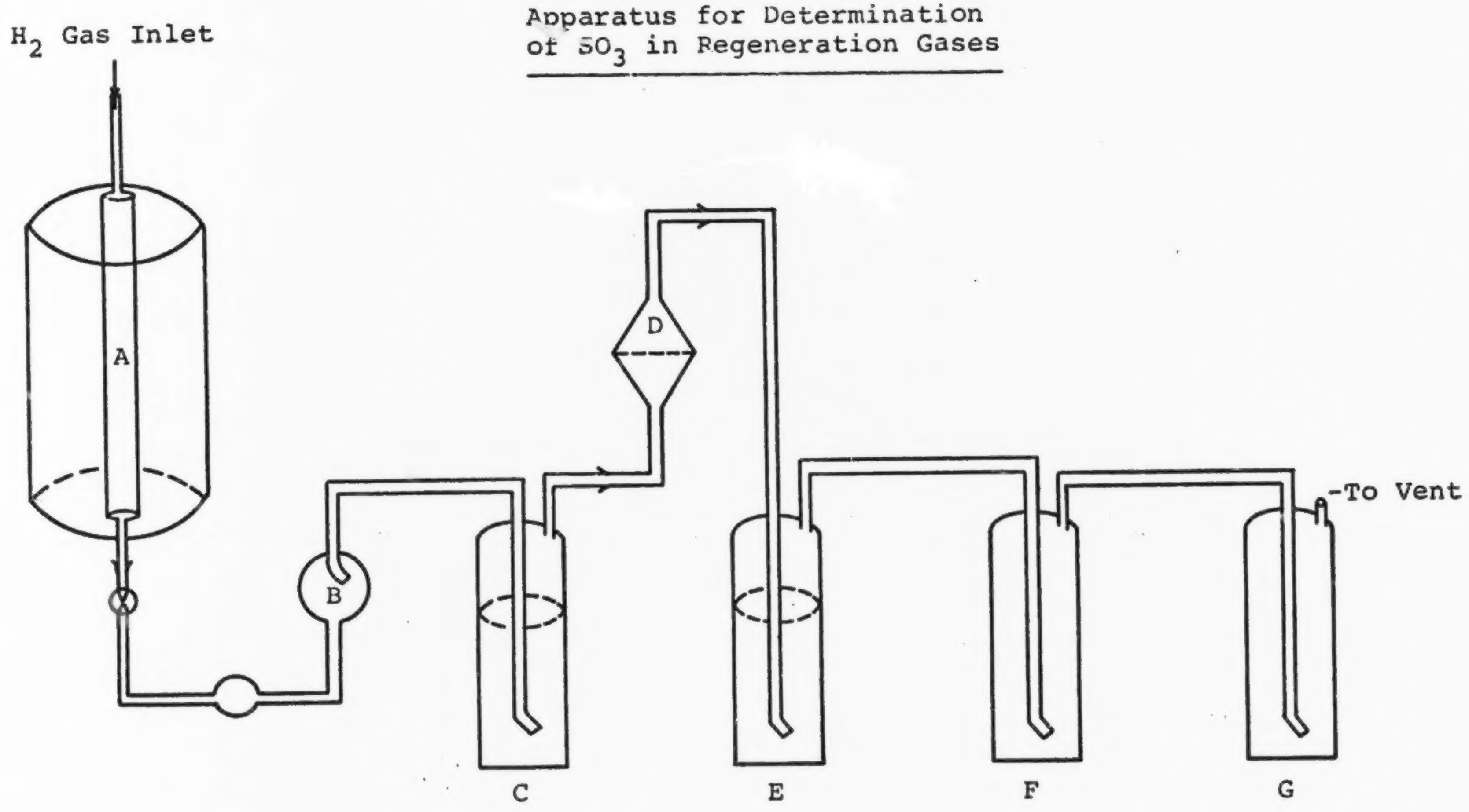
The SO_2-laden sample is placed inside an iron pipe that is heated by an electrically-wound furnace to between 500°C and 550°C. The desorption gas is passed downward through the sample. A heating tape keeps the exit line from the samples to the absorbers at about 300°C to prevent condensation of sulfuric acid. After the absorbing gas passes through the sample, it enters a scrubber, "B", where SO_3 and some SO_2 and H_2S are absorbed on 80% isopropyl alcohol. The gases leaving "B" are saturated with isopropyl alcohol vapor. Most SO_3 is present as sulfuric acid vapor or mist. The gas passes into absorber "C" where the balance of the SO_3 is converted to H_2SO_4. The free space above bottle "C" permits the growth of sulfuric acid mist particles to such a size that they are filtered out by the G-4 sintered glass filter shown as "D" in Figure V-1. At this point, all SO_3 is removed from the gas stream as sulfuric acid.

The gas then passes into bottle "E" where hydrogen sulfide is removed by reaction with cadmium acetate. The exit gas then goes to absorber "F", a starch-iodine solution that traps SO_2, and then to absorber "G", which contains sodium thiosulfate solution to trap any iodine that is carried out of absorber "F" by the sweep gases.

Each desorption is carried out for five hours. When terminated, the stop-cock on "B" is closed simultaneously with the shut-off valve that controls the flow of sweep gas through the sample. The 80% isopropyl alcohol solution in absorbers "B" and "C" is poured into a 500 cc gas bottle and scrubbers "B", "C", and "D" are rinsed several times with 80% isopropyl alcohol. These washings are also added to the 500 cc gas bottle. To this bottle is added 5 ml of concentrated hydrochloric acid and nitrogen gas is purged through the solution

FIGURE V-1

Apparatus for Determination of SO_3 in Regeneration Gases



A. Tube furnace around sample tube.
B. SO_3 absorption bulb, contains 40 ml isopropyl alcohol and 10 ml water.
C. SO_3 absorption scrubber, contains 160 ml isopropyl alcohol and 40 ml water.
D. G-4 sintered glass filter.
E. H_2S scrubber (5% cadmium acetate solution).
F. SO_2 scrubber (0.1N iodine solution).
F. Iodine trap (0.1N sodium thiosulfate solution).

for several hours to remove H_2S and SO_2 dissolved in the alcohol solution.

The gases are trapped in cadmium acetate and iodine, respectively, and the quantities of H_2S and SO_2 recovered from the isopropyl alcohol are added to those collected during the desorption. After the isopropyl alcohol solution is free of H_2S and SO_2, it is diluted to 500 cc in a volumetric flask and an aliquot portion is taken for sulfate analysis, determined by a standard barium sulfate gravimetric procedure.

Some SO_2 dissolves in the cadmium acetate solution used to collect the H_2S in bottle "E". To determine the H_2S trapped in bottle "E", the cadmium sulfide precipitate was filtered and washed rapidly with water. The filter paper with the precipitate was then dropped into standardized acidified iodine and the H_2S that formed when the precipitate dissolved was determined by back-titrating the iodine solution.

The filtrate from the cadmium sulfide filtration was also run into an iodine solution to react immediately without loss of SO_2 to the atmosphere, and the excess iodine was back-titrated with sodium thiosulfate. This SO_2 value was added to that determined in flask "F", as described below.

The SO_2 sorbed in flask "F" is determined by titration of the iodine with thiosulfate. The excess thiosulfate used in "G" is added to "F" and the amount of SO_2 is determined by back-titrating the excess iodine with sodium thiosulfate.